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4<sup>TH</sup> INTERNATIONAL CONFERENCE ON LANGMUIR-BLODGETT FILMS

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4TH INTERNATIONAL CONFERENCE ON LANGMUIR-BLODGETT FILMS

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DESIGNING OF A NEW L-B TROUGH TO CONTROL  
MOLECULAR ORIENTATION ON THE WATER SURFACE

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Recently much attempts have been made to prepare well ordered molecularly assembled thin films because they may have potential to guide molecular optics and electronics devices. A L-B technique is one of the methods to obtain thin films with thickness of molecular length. In a classical L-B technique, the problems associated with the machine and molecular aggregates above the water surface, are frequently encountered, thus it is difficult to obtain high quality L-B films. For example in an ordinary trough during the L-B film deposition process, (1) the monolayer is unhomogeneously compressed because of the friction between monolayer edges and walls of the trough. (2) the monolayer flows with shear from all sides of the trough to the solid substrate to fill a hole formed during deposition process.

In order to solve these problems, we designed a new LB trough<sup>1,2)</sup>, which has two unique characteristics. First, the width of the trough is kept same as that of the solid substrate to prevent the shear flow of the monolayer during the deposition. Secondly, both walls of the trough can move simultaneously with a barrier, therefore reduces friction between monolayer edges and walls to prevent a laminar flow of the monolayer. In fact, by our new L-B trough, stiff monolayer, such as aluminum stearate can be easily deposited on a glass substrate. The second main problem needs to be considered quality of monolayer on the water surface. We have also designed a zone heating system in the moving wall L-B trough. When cadmium stearate was spread on the water surface and compressed at the surface pressure of 30mN/m, it was observed that the area of monolayer decreases with the movement of the zone heater<sup>3)</sup>. The area change depends on both surface pressure and temperature increment by the zone heater. This implies that a folded structure of monolayer is formed on the water surface. Even the film formed by only one time deposition shows more clear and sharper X-ray diffraction pattern than L-B films obtained by ordinary L-B technique.

The third problem is how to orient monolayer. Sugi et al<sup>4)</sup>. demonstrated that anisotropic L-B films of the mixture of merocyanine and cadmium stearate was formed if the deposition

rate was increased. Employing this method, it is rather difficult to obtain uniform oriented L-B films on the whole substrate. Therefore, we attempted to design a new L-B trough which can control molecular orientation of monolayer on the water surface. The block diagram of the new trough is shown in figure 1. The trough is divided into three parts; a monolayer spread in wider area (a) is squeezed at the neck region (b) and deposit at (c). The Monolayer spread on wider area of the trough is squeezed at the neck region to flow to a substrate. The orientation of the monolayer can be achieved when passing through (b) region. The ratio( $l/l_0$ ) between the width of (a) and that of (c) is defined as compression ratio which corresponds to the draw ratio of solid polymer film.

Figure 2 shows the relationship between the dichroic ratio and compression ratio of the 5 layered merocyanine and cadmium arachidate mixture L-B film. Even if the deposition rate is very slow such as 5mm/min. in this experiment, the dichroic ratio increases with the compression ratio as shown in Figure 2. The dichroic ratio is uniform in the L-B film.

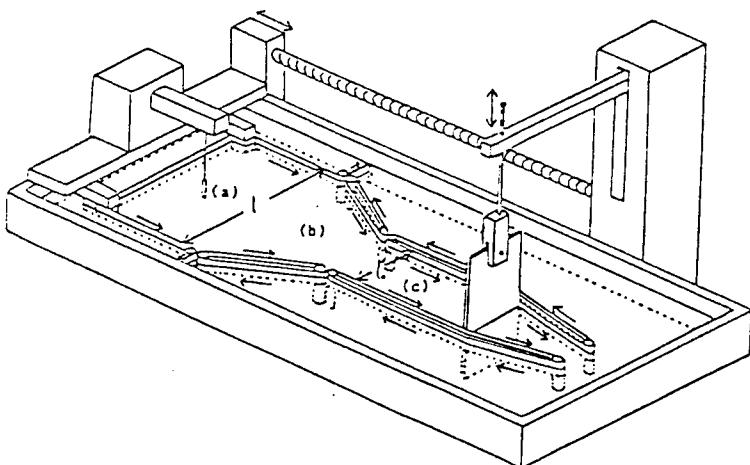


Figure 1. A block diagram of the new L-B trough to control molecular orientation of monolayer on the water surface.

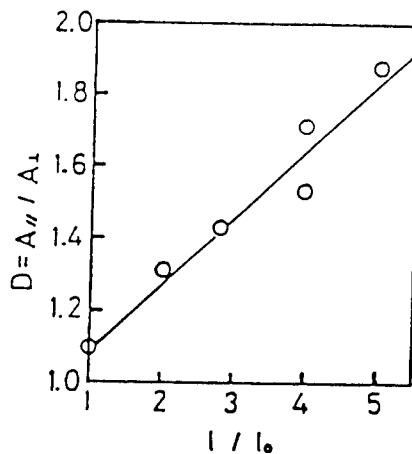


Figure 2. Plots of dichroic ratio at 600nm and compression ratio of the 5 layers of L-B film of merocyanine and cadmium arachidate mixture.

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Molecular Aggregation-Viscoelasticity Relationships  
of Monolayers at Air-Water Interface

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It is necessary for understanding the aggregation state of monolayers to evaluate the melting point  $T_m$  of them. In this study,  $T_m$  of monolayers prepared from fatty acids with different alkyl chain length was evaluated from the relation between subphase temperature  $T_{sp}$  dependence of the modulus and electron diffraction ED patterns of the monolayer at different  $T_{sp}$ , and also the aggregation state of those monolayers was investigated.

The magnitude of static elasticity( $K_s$ ) of a monolayer were evaluated from the  $\Pi$ -A isotherm by using the following equation.

$$K_s = -A(d\Pi/dA)$$

Figure 1 shows the  $T_{sp}$  dependence of  $\log K_{s(\max)}$  for stearic acid monolayers on the water surface and the ED patterns of its monolayers transferred at the surface pressure of  $20 \text{ mN}\cdot\text{m}^{-1}$ . The slope of the  $\log K_{s(\max)}$  vs.  $T_{sp}$  apparently changed at ca. 298 K. At the  $T_{sp}$  region lower than 298 K, the ED pattern showed the very sharp hexagonal spot of the crystalline state. On the other hand, at the higher  $T_{sp}$  region, the spots tend to be broad along the azimuthal direction with increasing  $T_{sp}$ , resulting in a Debye ring. This indicates that the molecular or crystallite orientation becomes poor with increasing  $T_{sp}$  above ca. 298 K. It was also observed that the thermal expansion coefficient of crystal lattice spacing  $d_{100}$  for stearic acid monolayer became large above 298 K. This crystallographic behavior is similar to that of the mechanical crystalline relaxation due to an increase in anharmonic potential term induced by a vigorous molecular motion<sup>1)</sup>. Further, the slope of  $\log K_{s(\max)}$  changed abruptly at ca. 317 K and the ED pattern at 318 K showed an amorphous halo. This indicates that the stearic acid monolayer at the air-water interface melts at ca. 317 K (the melting point at its bulk state was 342.6 K).

Figure 2 shows  $T_m$  of monolayers prepared from fatty acids

with different alkyl chain length which evaluated from  $T_{sp}$  dependence of  $\log K_s(\max)$ .  $T_m$  of fatty acids at a bulk state (by a DSC measurement) and of normal paraffin are also shown in fig.2.  $T_m$  of myristic ( $C_{14}$ ), palmitic ( $C_{16}$ ), and stearic acid ( $C_{18}$ ) at a monolayer state were ca. 278 K, 301 K, and 317 K, respectively. For the fatty acids with alkyl chain longer than that of stearic acid, it was difficult to evaluate the accurate  $T_m$  at a monolayer state because of equipment limitation for raising  $T_{sp}$ . However,  $T_m$  of monolayers prepared from fatty acids that consist of more than 20 number of carbon atoms were estimated along the broken line, for example, ca. 330 K for arachidic acid ( $C_{20}$ ) and ca. 340 K for behenic acid ( $C_{22}$ ).  $T_m$  at a monolayer state was lower than that at a bulk one, however, the temperature difference decreased with an increase of alkyl chain length.

In conclusion, the  $T_{sp}$  dependence of  $\log K_s(\max)$  was strongly related to the phase transitions of monolayers or thermal motion of amphiphilic molecules.  $T_m$  for monolayer can be evaluated from the measurement of  $\pi$ -A isotherms at different  $T_{sp}$ . It became apparent that melting point of the monolayer on the water surface was much lower than that at the bulk state.

Ref. 1) M.Takayanagi and T.Matsuo, J.Macromol.Sci.Phys., B1, 407(1967)

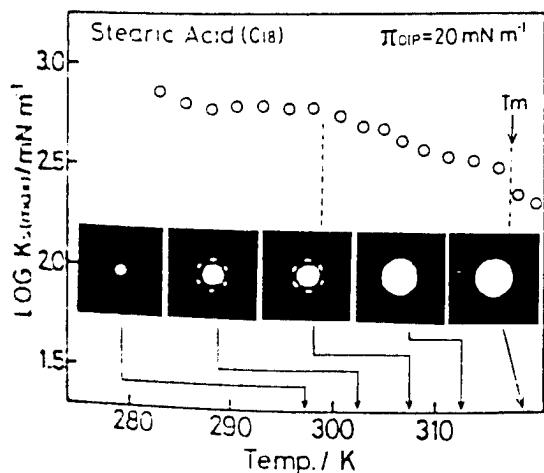


Fig.1.  $T_{sp}$  dependence of  $\log K_s(\max)$  and ED patterns of stearic acid monolayers

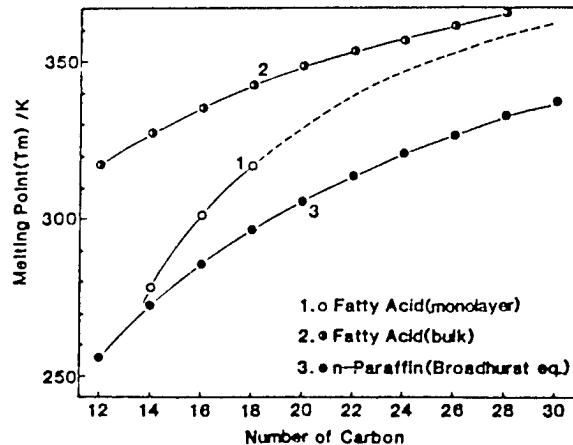


Fig.2.  $T_m$  of fatty acids with different alkyl chain length at a monolayer and bulk state.

## Improvement of LB Film Structure by Dynamic Surface Pressure Control

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It is well-known that a viscous monolayer on an aqueous subphase behaves inhomogeneously during compression in the LB method.<sup>1</sup> Actually, a large variation in surface pressure was quantitatively indicated by measuring the surface pressure at plural points over the subphase.<sup>2</sup> These results suggest that such a viscous behavior will cause a different inhomogeneity in the film deposition process. On the contrary, conventional deposition processes have been carried out on the uncertain assumption that the pressure over the whole surface was always kept constant at that of a Wilhelmy plate( $\pi_w$ ). Because the surface pressure at the substrate( $\pi_{sub}$ ) is a crucial factor affecting film transfer,<sup>3</sup> it is of fundamental interest to investigate the inhomogeneity in surface pressure during deposition. In this study, we directly evaluated the static( $\pi_{sub,s}$ ) and dynamic ( $\pi_{sub,d}$ ) surface pressures prior to and during substrate dipping, respectively, by measuring the external force imposed on the substrate.

For cadmium stearate which gives quite a low viscosity monolayer,  $\pi_{sub}$  hardly deviated from  $\pi_{sub,s}$  and coincided with  $\pi_w$  under a typical deposition condition. On the contrary, for a viscous monolayer of aluminum stearate, it was found that  $\pi_{sub}$  started to lower on substrate dipping and settled down at  $\pi_{sub,d}$ . Consequently, a considerable difference between them ( $\Delta\pi = \pi_{sub,s} - \pi_{sub,d}$ ) resulted during deposition, as depicted schematically in Fig.1. The difference,  $\Delta\pi$ , strongly depended on deposition conditions, such as the dipping speed, the distance between the substrate and the Wilhelmy plate, and the trough size. Figure 2 shows the variations in  $\Delta\pi$  as functions of the dipping speed and  $Al^{3+}$  ion concentration, a measure of the viscosity of the film.  $\pi_{sub,d}$  was found to be diminished to almost 0 dyn/cm on the condition that the dipping speed was 5 mm/min and  $[Al^{3+}]$  was  $1 \times 10^{-6} M$ .

A reduction in the difference,  $\Delta\pi$ , was found to be effective in

improving the film transfer characteristics, which was clarified by the structural characterization of multilayers formed by changing the magnitude of  $\Delta\pi$ . X-ray diffraction intensity analysis (Fig.3) and low accelerating voltage SEM images<sup>4</sup> indicated a marked improvement in film structure in accordance with the diminution of  $\Delta\pi$ .

Therefore, the above results suggest that an improvement in film structure can be attained by avoiding the monolayer flow on the subphase during the deposition process. Based on investigations of the conventional 'horizontal deposition method'<sup>5,6</sup>, in which the drop-on process causes no flow of the film, we have evolved a novel deposition method for a Y-type multilayer in the case of viscous monomolecular films and have confirmed the improvement of the film structure.

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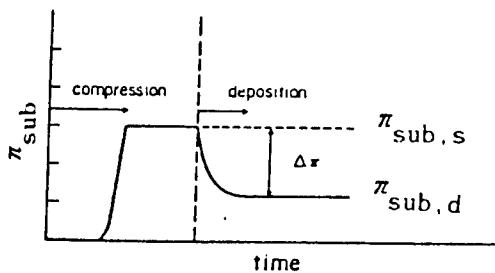


Fig.1 Change in surface pressure at substrate caused by deposition

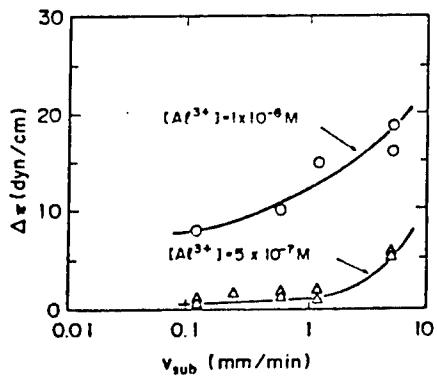


Fig.2 Changes in  $\Delta\pi$  observed for deposition of aluminum stearate monolayer with different  $Al^{3+}$  concentrations, at dipping speed ranging from 0.01 to 10 mm/min

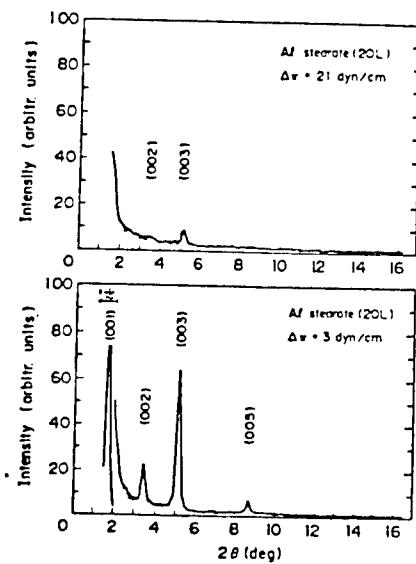


Fig.3 X-ray diffraction patterns of aluminum stearate multilayers (500Å), deposited by two methods giving different  $\Delta\pi$  ( $\pi_{sub,s} = 21$  dyn/cm); using usual trough ( $18 \times 30 \text{ cm}^2$ ), at dipping speed of 5 mm/min.  $\Delta\pi = 21$  dyn/cm (above); using modified trough equipped with two moving barriers ( $9 \times 6 \text{ cm}^2$ ), at dipping speed of 0.5 mm/min.  $\Delta\pi = 3$  dyn/cm (below)

# Structural Studies of Flavin Langmuir-Blodgett Films

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In order to realize the molecular electronic function with molecular organizations composed by electron transport proteins and/or their model LB films, it is very important to evaluate and control the molecular orientation. In this work, functional LB films based on flavin, which is typical of prosthetic groups for electron transport function in proteins, have been investigated on their fine structure by transmission electron microscopy (TEM) and on their molecular orientation by Fourier-transform infrared spectroscopy (FT-IR).

7,8-dimethyl-3,10-dinonylisoalloxazine (DNI) was used as a molecule for the flavin LB films(Figure 1). DNI monolayers were deposited on substrates by the vertical dipping method.

Figure 2 shows a dark field image of a monolayer film of DNI by TEM using a thin carbon film as a substrate. As shown in the figure, the film has a fibrous structure which consists of many planar fibrils oriented with an angle of about  $\pi/6$  to the dipping direction of the substrate. Such a fibrous structure has not been reported with respect to LB films of aliphatic acid<sup>1)</sup>, and could be characteristic for the LB film which has a biaxial functional group such as a flavin ring.

Figure 3 shows a transmission electron diffraction (TED) pattern of the same film as used in Fig.2. In this TED pattern, it is remarkable that all diffraction spots, which have symmetrical arcs, are aligned in lines normal to the direction of the fibrils. This result indicates that a unit of the fibril is a fibrous microcrystal with a particular crystalline axis (a fiber axis) ; the film has one dimensional crystallinity along the long axis of the fibrils which depends on the dipping procedure. Because of the good crystallinity deduced from the sharpness of the diffraction spots, it is concluded that DNI molecules take a very regular aggregation in the fibril.

Molecular orientation in the DNI LB films have been estimated by transmission and reflection absorption spectroscopy (RAS) measurements of FT-IR. The results showed that the long axis of the isoalloxazine rings orient almost parallel to the dipping direction.<sup>2,3)</sup>

Using a thin carbon film as a common substrate, TEM, FT-IR and XD measurements using a common substrate have also been performed. These results will further be discussed.

This work was supported by the MITI's Project of Basic Technology for Future Industries.

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Fig. 1 Molecular structure of DNI.

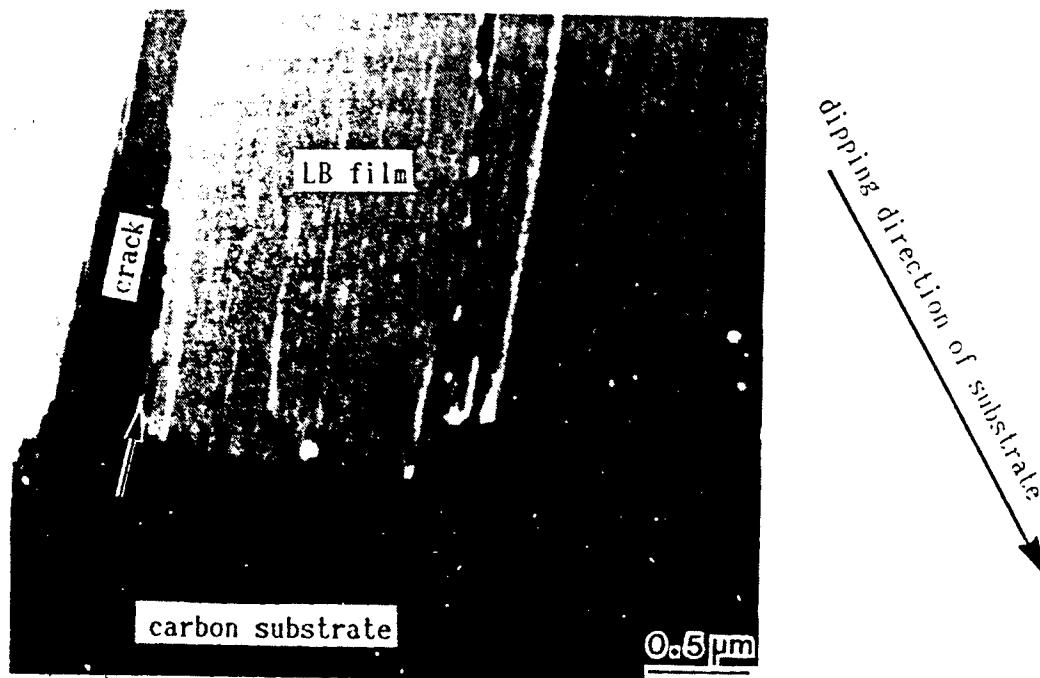


Fig. 2 Dark field image of a monolayer film of DNI by TEM.

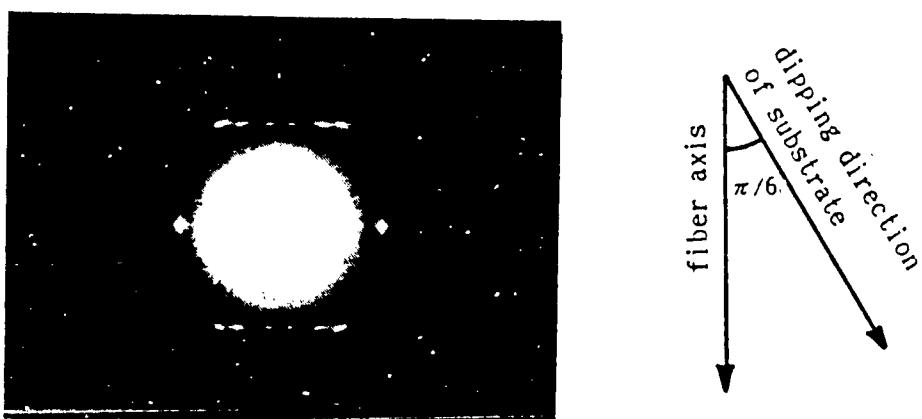


Fig. 3 TED pattern of a monolayer film of DNI (the same film as used in Fig. 2).

Characterization of LB films of Cadmium Stearate  
by Penning Ionization Electron Spectroscopy

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In Penning ionization electron spectroscopy, the kinetic energy of electrons ejected by collisions between targets T and metastable atoms  $A^*$  is analyzed:



Penning spectroscopy is selectively sensitive to the outermost surface layer of solids, since metastables do not penetrate into inner layers. Furthermore, an orbital of T extending outside the surface interacts with  $A^*$  more easily than an inner orbital and gives a stronger band in the Penning ionization electron spectrum (PIES). Thus, Penning spectroscopy provides information on the local electron distribution of individual orbitals exposed outside the outermost surface layer<sup>1)</sup>. Using these characteristics of PIES, we have studied the molecular orientation and electronic state of amphiphilic monolayers prepared both by the LB method<sup>2)</sup> and by vacuum sublimation<sup>3)</sup>. In this study the technique of PIES was further applied to cadmium stearate LB films to study the changes in the molecular orientation due to the increase in film thickness and also to thermal annealing.

The cadmium stearate monolayer was prepared from a benzene solution of stearic acid on water containing  $2 \times 10^{-4} \text{ M/l}$   $\text{CdCl}_2$  buffered with  $\text{NaHCO}_3$ . The first monolayer was transferred onto a silicon wafer by the vertical dipping (VD) method, while the following monolayers were deposited by the horizontal lifting (HL) method. In the HL method, after a face of the silicon plate was touched to the spread monolayer, a Teflon frame surrounding the plate was floated on the water surface to keep the residual monolayer away from the plate. Then the plate was lifted up from the water surface inside the frame. Therefore

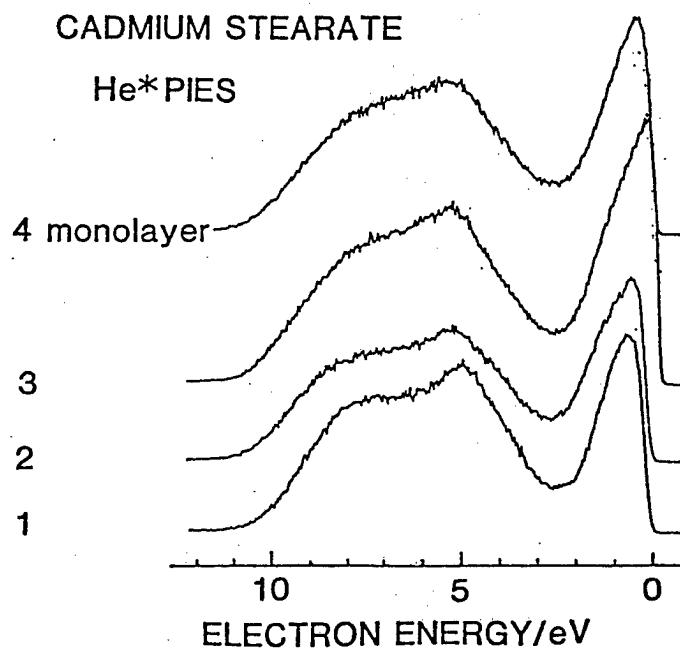


Fig.1  $\text{He}^*$  ( $2^3\text{S}, 19.82 \text{ eV}$ ) PIES of 1 to 4 monolayers of cadmium stearate.

the transfer ratio is considered to be unity.

Figure 1 shows the He<sup>\*</sup> PIES of 1 to 4 monolayers of cadmium stearate. Comparing the spectra of the cadmium stearate layers with that of an evaporated film of a long chain hydrocarbon, tetratetracontane ( $n\text{-C}_{44}\text{H}_{90}$ ) (Fig. 2), we find that the features of the spectra are quite similar with each other. Upon evaporation, long chain n-alkanes have been shown to form polycrystalline films with the chain direction perpendicular to the substrate surface (see the right of Fig. 2). In this case,  $\sigma$ -orbitals distributed mainly on the methyl end of the chain interact with He<sup>\*</sup> metastables more effectively than other orbitals to form the feature of the PIES shown in Fig. 2. Therefore, the close resemblance between the PIES of the cadmium stearate layers and that of the n-alkane film indicates that cadmium stearate molecules, irrespective of the number of layers, are oriented exposing their methyl ends outside the film surface. This result is consistent with a previous one obtained by the X-ray diffraction method: Cadmium stearate films prepared by the HL method have Y-type structure<sup>4)</sup>.

Figure 3 shows the temperature dependence of the PIES of a monomolecular film of cadmium stearate. Upon heating the film, the PIES showed a remarkable change around 90 °C (curve c), and the original spectrum (curve a) was not recovered after cooling back the film to room temperature (see curve d). This irreversible thermal change below the melting point of the sample (110 °C) is due to disordering of the hydrocarbon tails and has also been observed by Raman spectroscopy<sup>5)</sup>.

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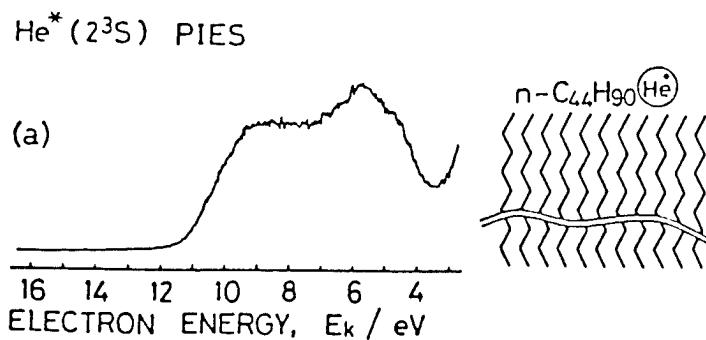


Fig. 2 He\*(2 S) PIES of an evaporated film of tetratetracontane ( $n\text{-C}_{44}\text{H}_{90}$ ).

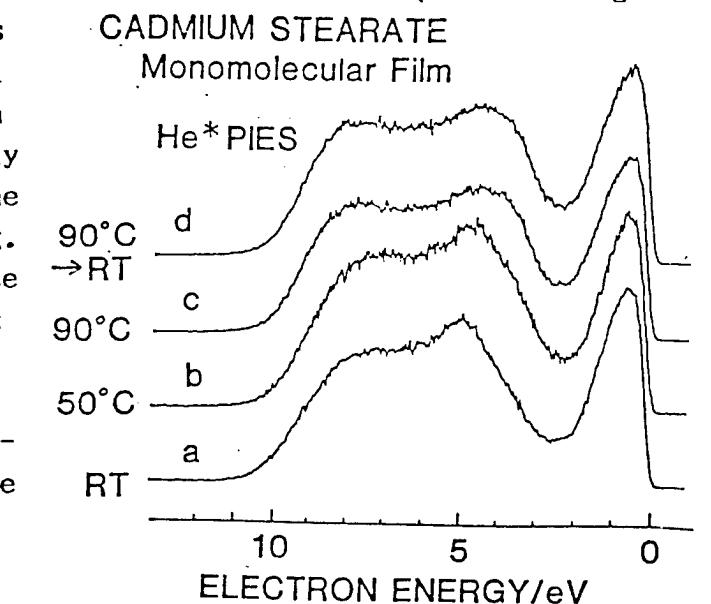


Fig. 3 Temperature dependence of He\*(2 S) PIES of a monomolecular film of cadmium stearate.

Novel Super Lattice Composed of  
Crystalline Monolayers and Amorphous Monolayers

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Many interesting applications of crystalline LB films have been already proposed and examined; Examples include the fabrication techniques that are possible only by the LB method, like polar structure fabrication for nonlinear optics<sup>1,2)</sup> and so on. Though the potential itself has been surely demonstrated, one of the major problems is the quality of film which often becomes crucial for applications. Crystalline LB films tend to have undesired heterogeneity such as void, domain and boundary, step and so on. In order to conquer the problem, we have investigated super lattice formation by use of alternating deposition of crystalline monolayers and amorphous monolayers.

The compounds used were an amphiphilic diacetylene of heptacosa-10,12-diyneic acid (14-8C)<sup>3)</sup> as a crystalline compound, and poly(isobutyl methacrylate) (PIBM)<sup>4)</sup> as an amorphous one. 14-8C was synthesized according to the literature<sup>3)</sup>. PIBM used was commercially available from Du Pont Co., Ltd. The trough and lifter used were specially designed one for hetero-deposition (FS-1, San-esu Keisoku), controlled by a personal computer. Subphase was aqueous solution of cadmium chloride ( $4 \times 10^{-4}$ M) and potassium hydrogencarbonate ( $5 \times 10^{-5}$ M). To compare the structure and the polymerization behavior of diacetylene moiety in multilayers, several types of hetero-deposition shown in Fig. 1 were examined. Pure multilayers were also prepared for comparison.

Polymerization of multilayers was stimulated by UV irradiation. Absorption spectral changes during polymerization of these hetero-deposited multilayers were similar to that of the pure 14-8C multilayer, though absorbance of the former was about half of that of the latter even at the same molar ratio of 14-8C. Under polarizing microscope, any textures from heterogeneity were not almost observable in hetero-multilayers, indicating that the optical scattering usually generated at the interface of crystal domains, voids and so on was suppressed.

To investigate the structures of these hetero-multilayers, X-ray diffraction analyses were carried out. Interlayer spacing of 14-8C was 6.05nm corresponding to the thickness of Y-type bilayer. Surprisingly, however, PIBM itself showed the diffraction patterns corresponding to the film thickness: Monolayer thickness by ellipsometry of PIBM was 1.01nm, The interlayer spacing of multilayer (3) was 8.51nm which is close to the summation of the bilayer thickness of the both components of 8.07nm. However, the multilayer (1) showed patterns just like those of pure 14-8C, though they were considerably weak. It seems that part of 14-8C penetrates through the PIBM layers to crystallize into bilayers either during deposition or after deposition. The diffraction patterns of multilayer (2) were more broad and obscure, but they were not fit to those of the pure 14-8C, indicating that interlayer penetration like in the multilayer (1) did not occur because of the thicker PIBM multilayers between 14-8C monolayers.

Thus, principal structures of super lattice with improved optical properties were realized. Further details of the major molecular orientations of 14-8C in these multilayers, examined by the methods other than X-ray diffractions, will be discussed.

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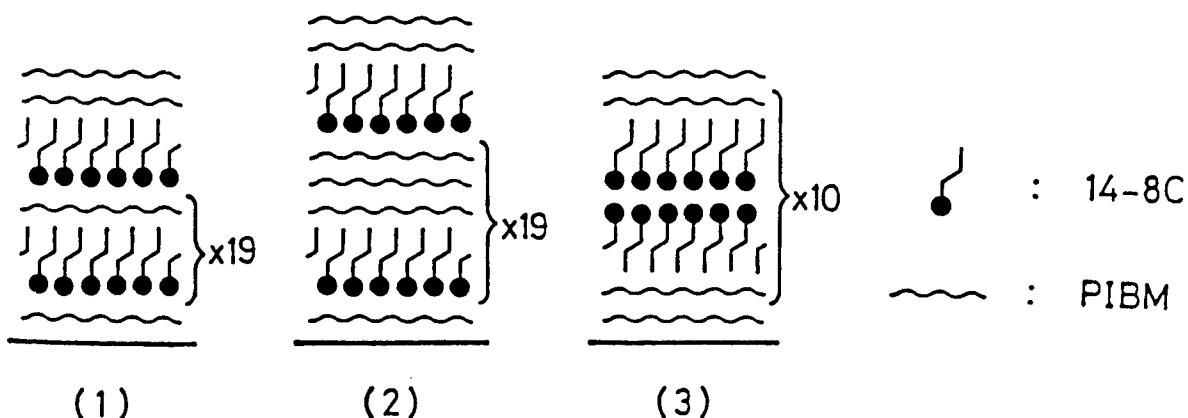


Fig. 1. Structural models of hetero-deposited multilayers composed of 14-8C and PIBM.

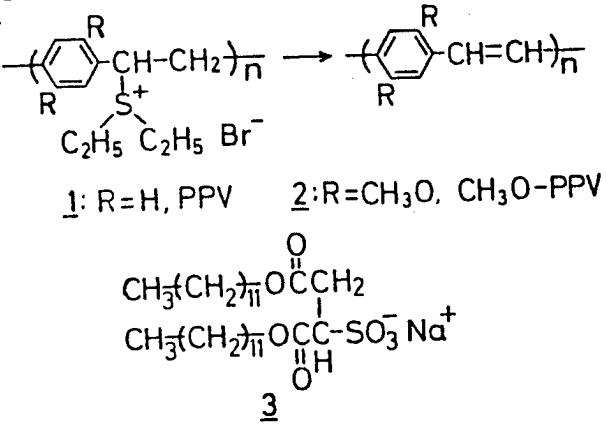
Preparation of Highly Oriented Polyarylenevinylene Thin Films  
by Using Langmuir-Blodgett Technique

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Polyarylenevinylenes (PAV) are attractive materials with high third order susceptibility and high conductivity. The PAV films are prepared by the thermal elimination of sulfonium group from the polyelectrolyte precursor films. We could prepared highly oriented PAV films utilizing a regulation of two-dimensional orientation of PAV precursors at the air-water interface.

Monolayers of a bilayer-forming amphiphile 3 were spread on aqueous solutions of polyarylenevinylene precursors (conc.= ca.  $10^{-4}$  M). The monolayers were compressed at  $30 \text{ mNm}^{-1}$  and were allowed to stand for about 4 hours to adsorb the precursors. The monolayers, which adsorb the precursors as counterions, were transferred on substrates by the conventional Langmuir-Blodgett (LB) technique. Finally, the precursor LB films were heated at  $100 - 200^\circ\text{C}$  for 1 hour under  $\text{N}_2$ .

Fig.1. is the absorption spectra of the Poly(p-phenylenevinylene) (PPV, 1) precursor LB film before and after the heat-treatment. A strong absorption appeared in visible region after the heat-treatment, demonstrating the formation of  $\pi$ -conjugated system (PPV structure) in the LB films. The absorption peak (460 nm) of PPV LB film is about 40 nm longer than that of the conventional PPV film obtained from the cast film of the precursor. The result indicates that mean  $\pi$ -conjugation length in the LB film extends, compared with that in



the conventional PPV film.

It was demonstrated from a linear dichroism of PPV LB film that PPV chains formed planar orientation in the film; dichroic ratio  $A_p/A_s$  decreased from 1.0 to 0.73 when the incident angle of polarized light increased from  $0^\circ$  to  $45^\circ$  (where  $A_p$  and  $A_s$  are absorbance of p- and s-polarized light at 460 nm, respectively). We suppose that the planar orientation originates in the formation of two-dimensional orientation of the extended polyelectrolyte precursor chains at the air-water interface in the adsorption process, and that the extension of mean  $\pi$ -conjugation length was realized owing to the high orientation.

Further, we could obtain a LB film of poly(2,5-dimethoxy-p-phenylenevinylene) ( $\text{CH}_3\text{O-PPV}$ , 2) by the same procedure. Extension of mean  $\pi$ -conjugation length and planar orientation of  $\text{CH}_3\text{O-PPV}$  chains in the LB film were also demonstrated from the absorption spectrum (Fig.2.) and the linear dichroism.

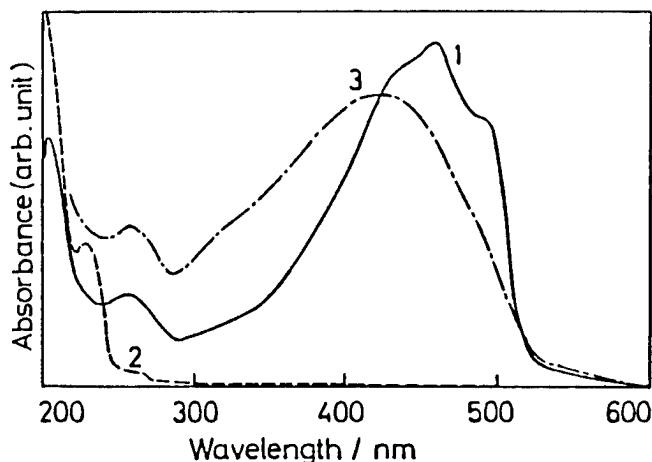


Fig.1. Absorption spectra of PPV LB film (line 1) and the precursor LB film (line 2). Line 3 is a spectrum of the conventional PPV cast film.

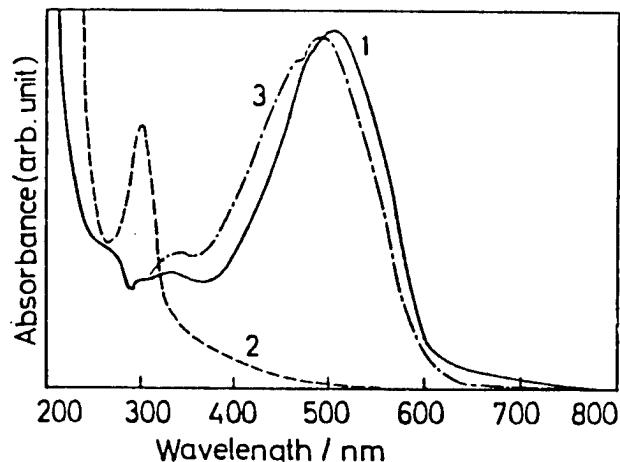


Fig.2. Absorption spectra of  $\text{CH}_3\text{O-PPV}$  LB film (line 1) and the precursor LB film (line 2). Line 3 is a spectrum of the conventional  $\text{CH}_3\text{O-PPV}$  cast film.

Photopolymerization of Long-chain Diacetylene Monocarboxylic Acid  
in LB Films Studied by UV Photoelectron Spectroscopy (UPS) and X-  
ray Absorption Near Edge Structure (XANES)

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Many diacetylene compounds  $R-C\equiv C-C\equiv C-R'$  are known to polymerize under UV irradiation to form extended  $\pi$ -electron systems. Further, some polymers undergo transitions between the so called "blue" (B) and "red" (R) forms by elongated UV irradiation, thermal treatment, or mechanical stress. The B and R forms were at first ascribed to the two possible ways of conjugation, i.e. acetylenic (Ac) and butatrienic (Bu) forms

$\{CR-C\equiv C-CR'\}_n$  (Ac)                     $\{CR=C=C=CR'\}_n$  (Bu), respectively [1], but an alternative assignment was proposed to the red form [2], based on the contradiction between the observed and theoretically calculated (butatrienic form) band gaps.

On the other hand, the electronic structure of polydiacetylene is not yet well understood. The extensively studied optical properties contain combined contribution from occupied and vacant states. Further, most previous works on polymers with  $\pi$ -containing pendants were hindered by the overwhelming contribution from the side groups ( $R$  and  $R'$ ) overlapping to that from the main-chain  $\pi$ -systems [3]. Fortunately, long-chain diacetylene monocarboxylic acids  $R = CH_3(CH_2)_n$ ,  $R' = (CH_2)_mCOOH$  in LB and evaporated films can be used for such a study, without perturbation from the side groups to the upper  $\pi$ -electronic states in the main chain.

In this work, we investigated the change of the electronic structure of tricoso-10,12-diynoic acid ( $n = 9$ ,  $m = 8$ ) on UV irradiation by UV photoelectron spectroscopy (UPS) and X-ray absorption near edge structure (XANES) for probing the occupied and unoccupied states, respectively. The XANES spectra of the monomer [4] and polymer [5] have been reported separately, but the continuous change from the monomer to the polymer nor the difference between the blue and red forms have not been studied.

In UPS measurements [6], LB films up to 5 layers of various degrees of polymerization were studied. The UPS spectra for  $h\nu = 8.16$  eV are shown in Fig. 1. Reflecting the formation of extended  $\pi$ -electron band upon polymerization, the ionization threshold energy was decreased from 6.7 eV (monomer) to 5.1 eV for both the blue form (after short irradiation) and the red form (after long irradiation). Theoretical calculations [7] indicate that

the ionization energies of the acetylenic and butatrienic forms should be different by ca. 1 eV. The lack of difference between the observed values of the blue and red forms suggests that the polymer chain is in the acetylenic form in both forms.

In the XANES measurements, both evaporated films (free acid) and LB films (Cd salts) were studied. Figure 2 depicts the spectra of more extensively studied evaporated film in the photon energy region of C 1s excitation region. The sharp peaks A to C correspond to the carbon  $1s \rightarrow \pi^*$  transitions. The single peak in the monomer is split by polymerization. This should correspond to the change from two conjugated triple bonds to isolated triple bonds and the evolution of the density-of-states of an extended 1-dimensional unoccupied  $\pi^*$  band. Possible assignments of these peaks will be discussed with the aid of theoretical calculations.

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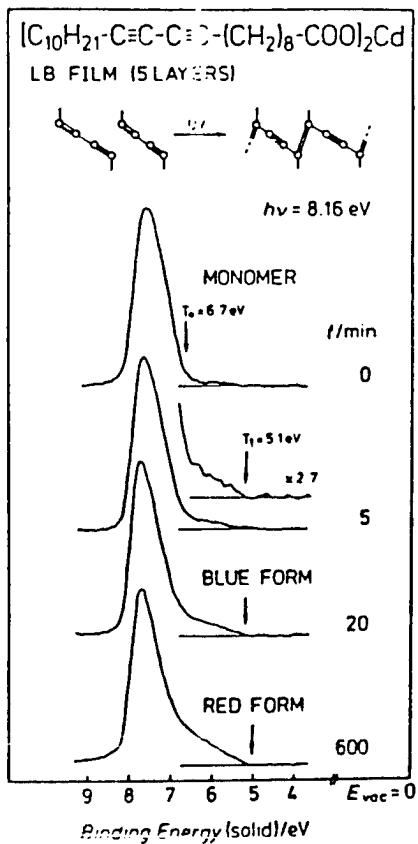


Fig. 1 (Left) Change of the UPS spectra for LB films at  $h\nu = 8.16$  eV on polymerization. The time of UV irradiation is shown for each spectrum.

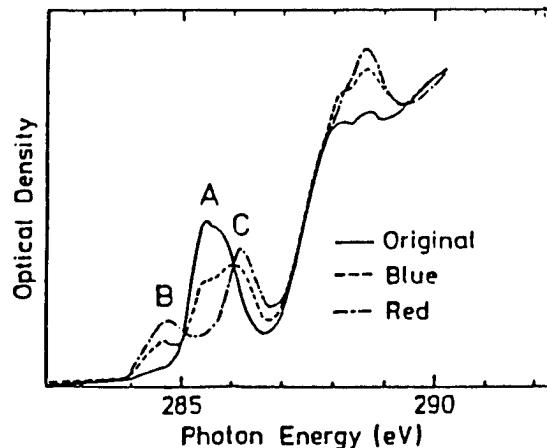


Fig. 2 Change of the C 1s XANES spectrum of an evaporated film on UV irradiation.

# ELECTRICAL MEMORY-SWITCHING IN LANGMUIR-BLODGETT FILMS

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It was widely accepted that Langmuir-Blodgett ( LB ) films never were prepared on hydrophobic substrates, i.e. noble metals such as Au and Pt, without structural defects being formed and acting as nuclei for a filamentary conduction in the films [1]. Recently, it has been barely recognized that some LB films have a fairly small number of defects, even on a noble metal electrode [2], where the presence of oxide layer is avoidable in contrast to a prevalent Al electrode. Consequently, as we reported in the outline previously [3], a novel electrical switching phenomenon was observed in the LB films having a metal-film-metal sandwich structure.

Figure 1 shows a typical switching behavior of 12 monolayers (18 nm thickness) of squarylium dye sandwiched between top-Al and base-Au electrodes. A voltage is applied across a  $100\ \Omega$  load resistor and the film with the top electrode biased positively. Upon the application of a certain voltage, the film switches from a non-conducting OFF state (non-ohmic,  $> 10^6\ \Omega$ ) to a conducting ON state (ohmic,  $20 - 100\ \Omega$ ). Although the ON state is maintained when the voltage is subsequently reduced, it could be returned to the OFF state by applying a voltage above the threshold value. This memory switching occurs reproducibly.

As shown in Fig.1, switching behavior is unsymmetrical with regard to the applied voltage: Switching from the OFF to ON state occurs via an intermediate state contrary to switching back to the OFF state directly, and the intermediate state is developed only when the top electrode is biased negatively. In the case of Au-film-Au symmetrical structures, switching observed is symmetrical.

Moreover, the study employing a metal ball as a top electrode has been performed.

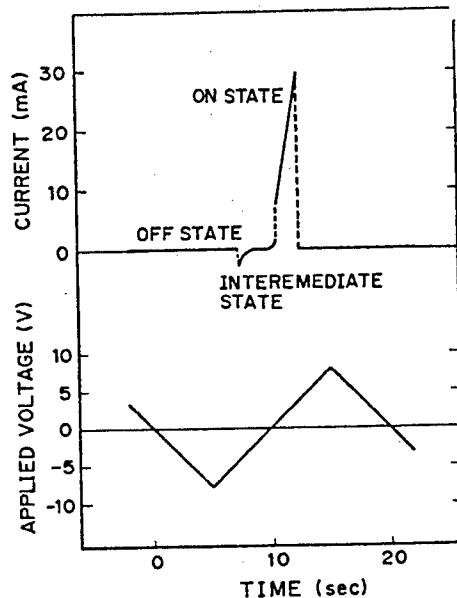


Figure 1.  
Switching behavior of a 18 nm film of  
Al-squarylium-Au sandwich structure,  
where a load resistor is  $100\ \Omega$ .

The structure is composed of a stainless ball ( 2 mm in diameter ) covered with evaporated Au film that comes in contact with the surface of LB film prepared on a base-Au electrode; As a result, memory switching also occurs, however the effect is highly unstable. Switching behavior is similar to that of the above-mentioned Au-film-Au structure. This is important in practical applications, since it suggests that a movable probe can access the objective point in the LB film, where switching to ON ( WRITING operation ) or switching back ( ERASE ) is possible by applying a voltage.

The resistance of the film has evident linear dependence on the film thickness, in either case of OFF and ON state [3]. In addition, the electrical field and potential measurement with an Al electrode interposed in LB films, i.e. a metal-film-metal-film-metal structure, shows that the potential distribution in LB films is only slightly changed before, during, and after the switching ( see Fig.2 ). The obtained results indicate that the conduction is due to the region of LB films ( bulk LB film ), and exclude the possibility of the presence of filamentary pathways.

At present the mechanism responsible for switching is uncertain. However, an electrical change in the bulk LB films, such as the field-induced intramolecular structural change in conjugated system [3], is very likely to dominate the phenomenon. We believe that feasibility of future devices utilizing LB films, has been demonstrated.

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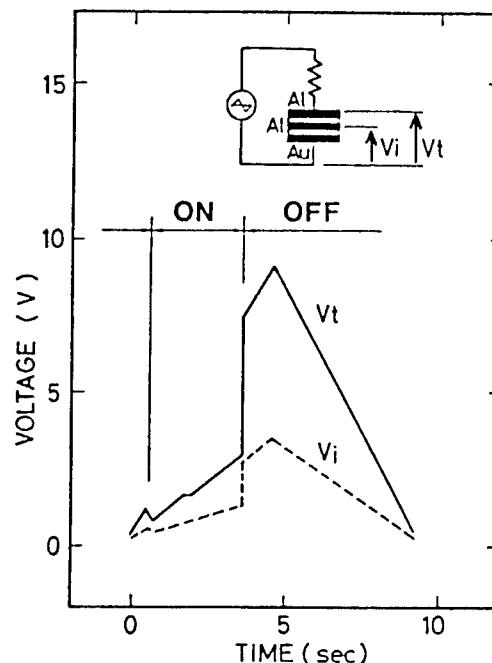


Figure 2.  
Variations of the top-electrode potential  $V_t$  ( solid line ) and interposed-electrode potential  $V_i$  ( dashed line ) during the switching.

# Low-Energy Electron Transmission Through Langmuir-Blodgett Films of Cadmium Arachidate

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Langmuir-Blodgett (LB) films are of an attractive interest in various fields because of good orientation of molecules in the films. However, the molecular orientation and its correlation to the electronic structure in these films have not yet been well understood. Further, the effects of electron-phonon coupling on the electronic structure, which have generally been neglected in discussing the temperature dependence of their electrical properties, have not been studied.

Low-energy electron transmission (LEET) experiment is very powerful in investigating conduction bands and hot-electron transport in thin films of solids [1]. Further, we can obtain the information of molecular orientation, crystallinity of the films as well as the conduction band structure, since the band structure correlates strongly to the crystal structure of the film. We present LEET results for Cd-arachidate, and show the direct determination of the bottom of the conduction bands in the alkyl chains, the effects of the molecular vibrations (phonon) on the band structure and the effects of molecular orientation on the LEET spectra.

Figure 1 illustrates the principle of LEET experiment, where a monoenergetic electron beam of low current density is injected to the film deposited on a metal substrate and the electron current transmitted through the film ( $I_t$ ) is measured in ultrahigh vacuum as a function of incident electron energy ( $E_i$ ). Therefore, one may consider "vacuum" as a well-understood "electrode" contacted onto the film surface.

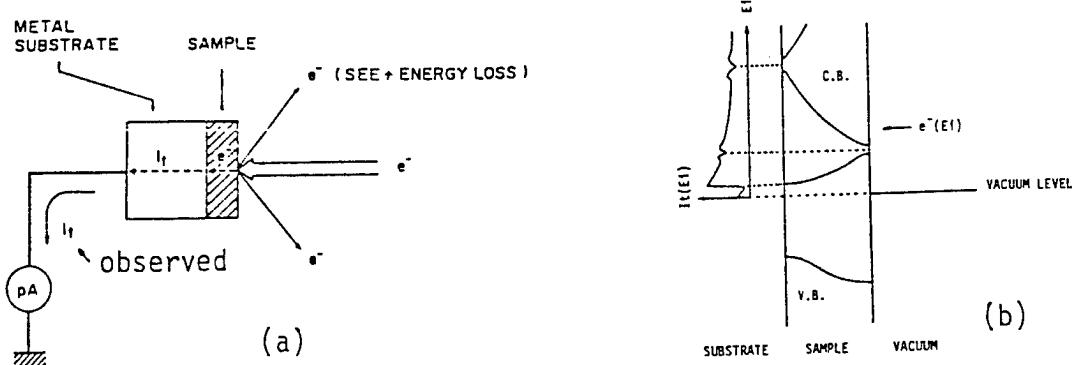


Fig. 1 Schematic illustrations of low-energy electron transmission experiment (a) and an origin of  $I_t$  structure (b).

Figure 2 displays LEET spectra ( $I_t$  and  $dI_t/dE_i$ ) of the 2L, 4L, 6L and 8L films at low temperature. The small shoulder near 0 eV is electron transmission through the band gap. The large increase of  $I_t$  at 0.5 eV correspond to the onset of the electron injection to the conduction band. Thus, the bottom of conduction band derived by long-alkyl parts is directly determined to be  $0.46 \pm 0.02$  eV above the vacuum level. This value depended on both crystallinity and temperature, and it was smaller than 0.46 eV at room temperature and for a film of low crystallinity.

Other examples of LEET spectra are shown in Fig. 3 for oriented and unoriented films. The unoriented film was obtained by a heat treatment similar to that used in angle-resolved photo-emission experiment [2]. It is understood from the comparison that the remarkable dip feature in  $I_t$  curve or the intense peak in  $dI_t/dE_i$  curve around 10 eV reflect the perpendicular orientation of alkyl chains.

The effects of molecular vibrations and aging effects will be also presented as well as thickness dependence of the orientation.

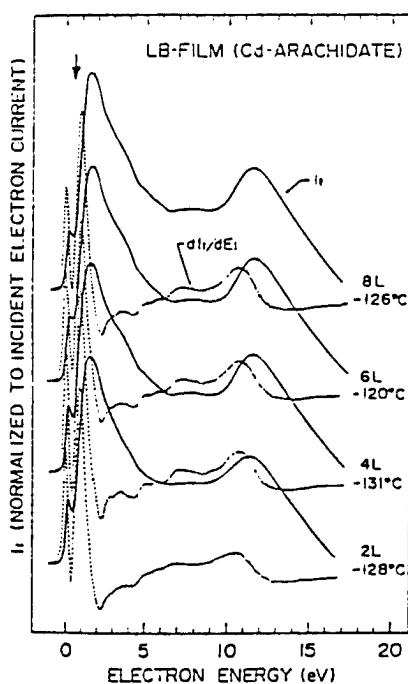


Fig. 2 Low-energy electron transmission spectra ( $I_t$  and  $dI_t/dE_i$  curves) for 2L, 4L, 6L, and 8L LB-films of Cd-arachidate at low temperature. The incident electron current was  $1 \times 10^{-11}$  A. The bottom of conduction bands in alkyl chains is indicated by arrow.

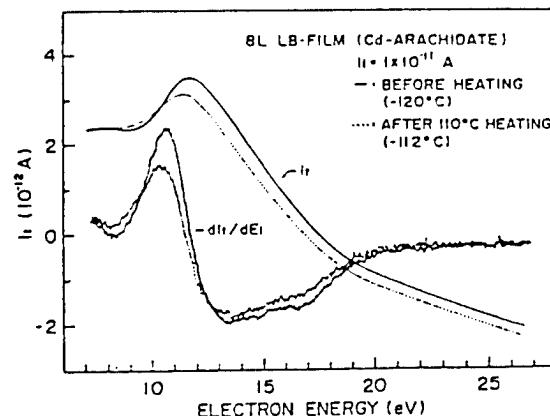


Fig. 3 Effects of molecular orientation on low-energy electron transmission spectra at higher energy region. After 110 C heat treatment, the perpendicular orientation of the alkyl chain is destroyed (see ref. 3).

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Anomalous Linewidth of Electron Spin Resonance in  
Langmuir-Blodgett Films of the 3:2 Complex of  
Tetramethyltetrathiafulvalene and  
Tetradecyltetracyanoquinodimethane

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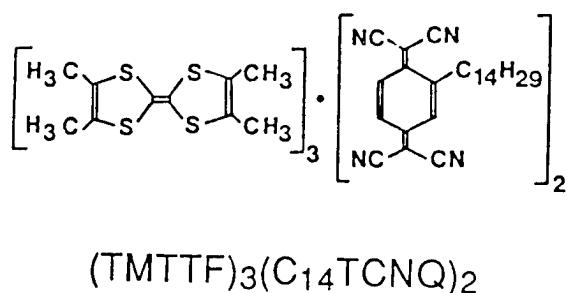
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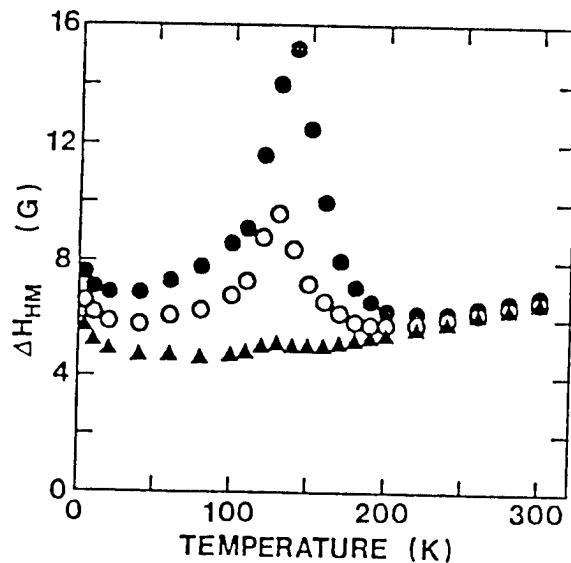
Langmuir-Blodgett (LB) films of the 3:2 complex of tetramethyltetrathiafulvalene and tetradecyltetracyanoquinodimethane (Fig. 1, referred to as  $(\text{MTTF})_3(\text{C}_{14}\text{TCNQ})_2$ ) exhibit a high bulk conductivity ( $\approx 1 \text{ S/cm}$ ) as a stable monolayer system.<sup>1)</sup> The electron spin resonance (ESR) technique was applied upon this system and the possible occurrence of Peierls fluctuations around 150 K has been already reported.<sup>2)</sup> It was suggested that the fluctuating charge density waves were pinned by the disorders in the system, or so called "interrupted strands", below 100 K.

The fluctuations mentioned above can be characterized by the observed maximum of the temperature-dependent ESR linewidth as shown by the filled circles in Fig. 2. We report here that the maximum of the linewidth are reversibly affected by the pressure of the atmosphere in which the samples were sealed. ESR linewidth of the sample sealed with 860-torr helium gas showed a clear maximum around 150 K (Fig. 2, filled circles), while that of the sample sealed with 10-torr helium gas showed no such clear anomaly (Fig. 2, triangles). The pressure of 860-torr is quite low if one compare it with the pressure at which drastic changes in electronic properties occur in the crystalline system of some organic metals such as pressure-induced CDW or SDW transitions, suggesting that the LB film system is more easily controllable.

The temperature dependence of the linewidth was almost the same regardless of the conditions whether the temperature was being decreased or increased, or being decreased rapidly or slowly. The mixture of other gas species such as oxygen or nitrogen with helium confirmed that the total pressure of the atmosphere, not the composition of it, is responsible for the phenomenon described above.



**Fig. 1** Chemical structure of  $(\text{TMTTF})_3(\text{C}_{14}\text{TCNQ})_2$



**Fig. 2** The temperature dependence of the ESR linewidth observed for LB films sealed with 860-torr(●), 460-torr(○) and 10-torr (▲) helium gas.

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## Conductive Langmuir-Blodgett Films Based on Alkylammonium-M<sub>i</sub>(dmit)<sub>2</sub> Complexes

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Conductive Langmuir-Blodgett (LB) films reported so far are classified as one-dimensional organic conductors, which are very sensitive to the defects in the conduction stacks and have intrinsic instability as one-dimensional system. By the introduction of higher dimensionality, this instability can be suppressed and higher conductivities will be realized.

We report here the synthesis, structural characterization and electrical conductivity studies of LB films of metal-(dmit)<sub>2</sub> complexes. This sulfur-rich 1,2-dithiolene complex has provided three kinds of molecular superconductor, TTF[Ni(dmit)<sub>2</sub>]<sub>2</sub>, TTF[Pd(dmit)<sub>2</sub>]<sub>2</sub> and Me<sub>4</sub>N[Ni(dmit)<sub>2</sub>]<sub>2</sub>.

Amphiphilic ammonium salt of the metal-(dmit)<sub>2</sub> complexes are synthesized according to the procedures described previously.<sup>1)</sup> Dialkyldimethyl- or trialkylmethyl-ammonium and Ni or Au was used as a counter cation and a central metal cation, respectively (Fig. 1). The 1:1 mixtures with icosanoic acid formed monolayers at the air-water interface. These monolayers were transferred onto a solid substrate and converted to the conductive LB films by the oxidation of bromine gas or the electrooxidation in the LiClO<sub>4</sub> aqueous solution. The bulk conductivity of the bromine-oxidized films of 2Cn-M is summarized in Fig. 2.

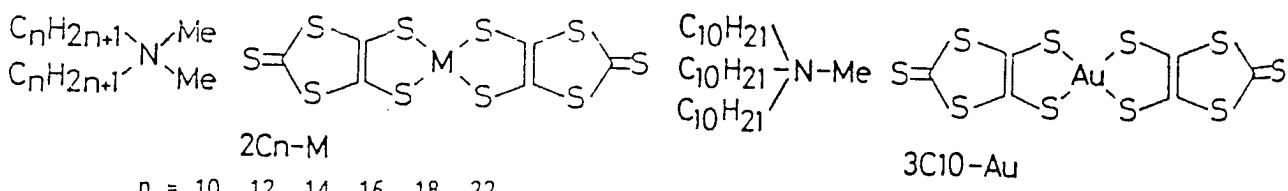


Figure 1.

Fairly conductive LB films were obtained by the use of 3C10-Au.<sup>2)</sup> The bulk conductivities of the oxidized films were ca. 10 S/cm for bromine oxidation and ca. 30 S/cm for electrooxidation. Figure 3 shows the temperature dependence of electrical conductivity of 3C10-Au LB film after electrooxidation measured by dc 4-probe method. The film was metallic down to 200 K with weak temperature dependence. Below 200 K, the film showed the activation-type conductivity. The film still exhibits the conductivity of ca. 10 S/cm at 10 K suggesting that the metal-insulator transition does not occur in this temperature region.

In summary, we have prepared for the first time highly conductive LB films exhibiting metallic temperature dependence of conductivity.

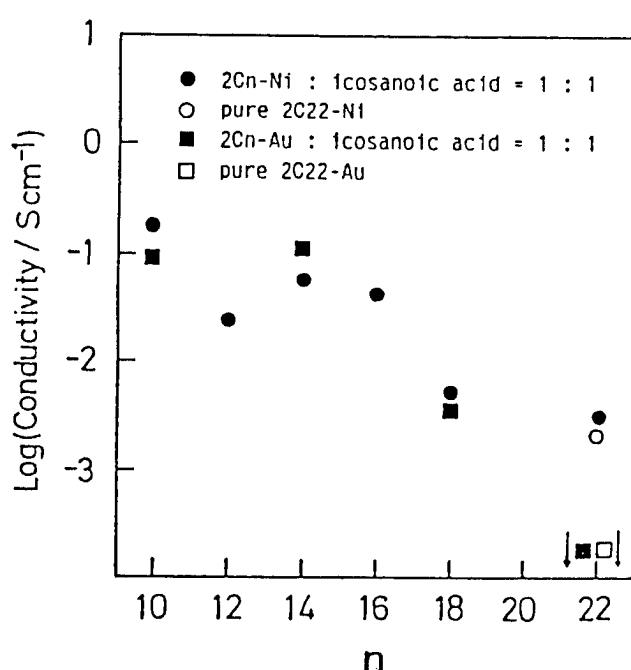


Figure 2.

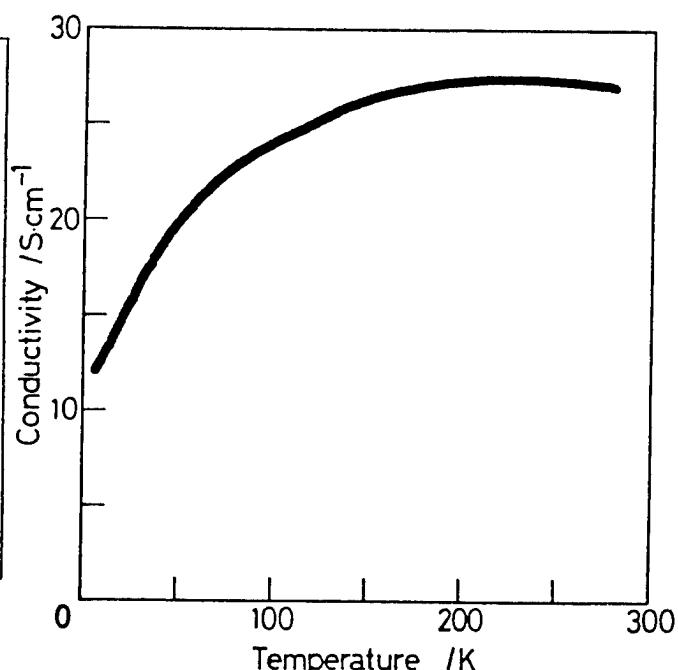


Figure 3.

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\*\*On leave of absence from Toyo Gosei Kogyo Co., Ltd., Funabashi, Chiba 273, JAPAN.

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Preparation and Properties of Poly(p-phenylene vinylene)  
LB Films

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We have reported the preparation of ultra-thin films of polyimides and poly(p-phenylene vinylene)s (PPV) using Langmuir-Blodgett (LB) technique.<sup>1-4)</sup> Because these condensation polymers were neither amphiphilic nor hardly soluble in organic solvents, a new preparative method for polymer LB films, "Precursor Method", was developed. The "Precursor Method" consists of three steps, 1) preparation of monolayer film of amphiphilic precursor polymers having long alkyl chains at air/water interface, 2) deposition of the monolayer films onto a substrate, 3) conversion of the precursor polymers by appropriate treatment to the multilayer film of target polymers with removal of the long-alkyl chains.

Electrically conductive LB films are one of the most fascinating targets in the LB field and several attempts have been made to monomeric and polymeric conducting LB films<sup>5)-9)</sup>. But they had the anisotropic conducting nature because of the existence of insulating alkyl chains. On the multilayer films of PPV prepared by use of the "Precursor Method", more isotropic nature should be expected. In this paper, we report the electric and electrochemical properties of PPV multilayer films prepared by the "Precursor Method".

We chose poly(sulfonium salt) 2b having perfluorononanoate counter ion as the amphiphilic precursor of PPV. Fig. 1 shows the  $\pi$ -A curve of 2b. The monolayer film of 2b could be deposited onto various plates through the Y-type deposition. The multilayer films of 2b were subsequently converted to multilayer film of PPV 3 by thermal treatment ( $200^{\circ}\text{C}$ , 2 h) under vacuum where perfluorononanoic acid spacer group were removed from 2b.

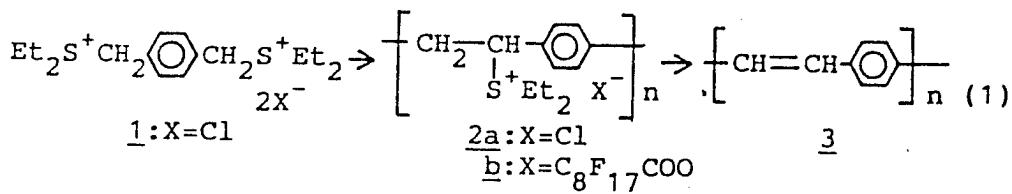
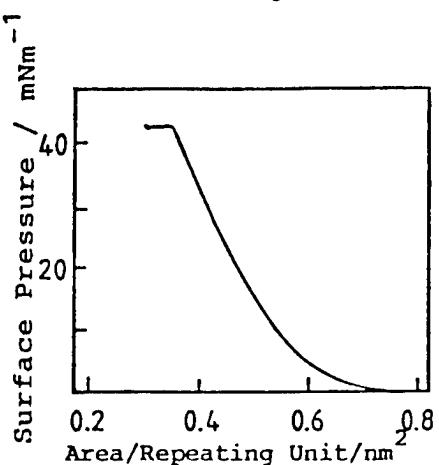
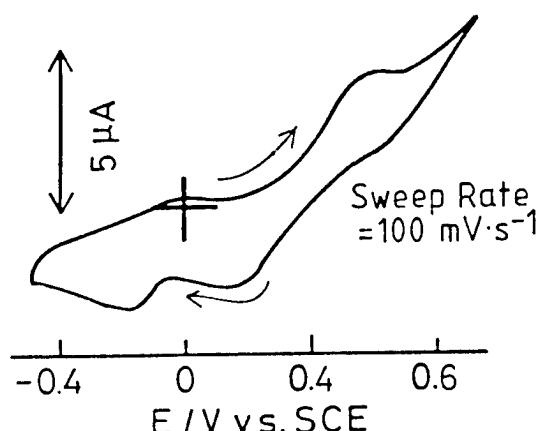


Figure 2 shows the current-voltage characteristics measured in ITO/PPV multilayer film/Au system. The conductivity of multilayer film of 3 in the undoped state was about  $10^{-16}$  S/cm for the normal direction of the film, whereas it was at least  $10^{10}$  times enhanced by doping with  $\text{SO}_3$ . The conductivity of the  $\text{SO}_3$  doped film for the lateral direction was 0.5 S/cm, which was comparable to the value of usual PPV film<sup>10)</sup>.

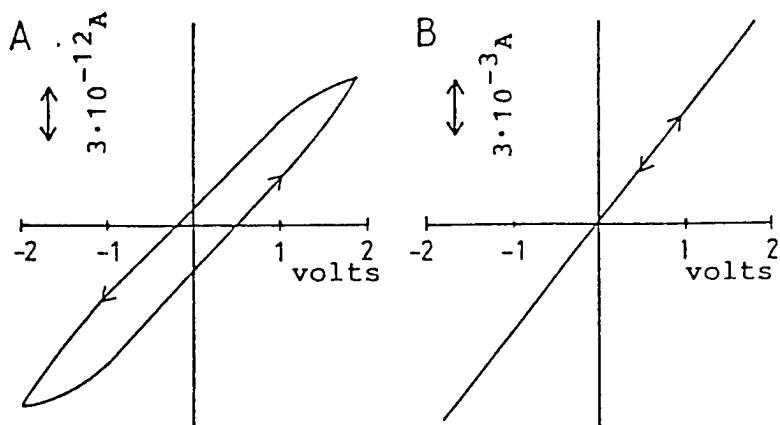
In the next stage, electrochemical behavior of the PPV LB film was examined. Figure 3 shows a cyclic voltammogram of the PPV LB film (deposited on a gold electrode) measured in acetonitrile solution containing 0.1M  $\text{KFP}_6$  as a supporting electrolyte.



(Fig. 1) Surface Pressure-Area Isotherm of 2b



(Fig. 3) Cyclic Voltammogram of PPV LB Film deposited on Gold Electrode (10 Layers)



(Fig. 2) Current-Voltage Characteristics of ITO/PPV LB Film/Au Sample.  
A: Undoped PPV Film (300 Layers), B:Doped with  $\text{SO}_3$ .

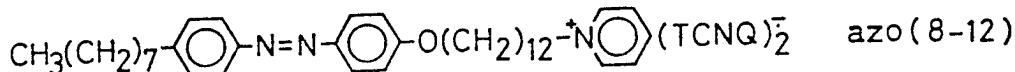
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# PHOTORESPONSIVE CONDUCTIVITY IN LANGMUIR-BLODGETT FILMS

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Photochromic Langmuir-Blodgett (LB) films have recently attracted much interest from the viewpoint of high-density optical memories. Reversible photochromisms based on cis-trans isomerization,<sup>1,2</sup> spiropyran-merocyanine isomerization,<sup>3</sup> dimerization,<sup>4</sup> and redox reaction<sup>5</sup> are reported. Photoisomerization of a molecule cause a structural change of the other parts of the LB films. Therefore, it is feasible that the photoisomerization in the LB films can control the functions of the films, the functions for which the other parts of the amphiphiles are responsible. In this respect, we have introduced photochromic moiety into the amphiphilic charge transfer (CT) complex.



Amphiphilic CT complex containing azobenzene group, azo(8-12), was synthesized. Figure 1 shows photochromic properties of the LB film. The absorbance of trans-azobenzene around 356 nm decreases on irradiation at 365 nm, while that of cis-isomer around 450 nm increases ((a)→(b)). The cis-to-trans isomerization of azobenzene occurs on irradiation at 436 nm ((b)→(c)). The change of absorption spectra was reproducible in further irradiation cycles ((b)↔(c)), although the spectrum (c) is slightly different from the initial one (a).

The change in the absorbance of the trans-azobenzene at 356 nm and the conductivity of the LB film under nitrogen atmosphere is shown as a function of irradiation time in Fig. 2. It is clear

that the increase of the conductivity is accompanied with the trans-to-cis photoisomerization ( $\lambda_1 = 365$  nm) of azobenzene and that the conductivity reverts to the initial state with the cis-to-trans isomerization ( $\lambda_2 = 436$  nm). The change of the conductivity was reversible more than one hundred times. The half life of thermal recovery of the cis-to-trans isomerization was almost equal to that of the conductivity at room temperature. These results show that the change of the conductivity is induced by the photoisomerization of azobenzene.

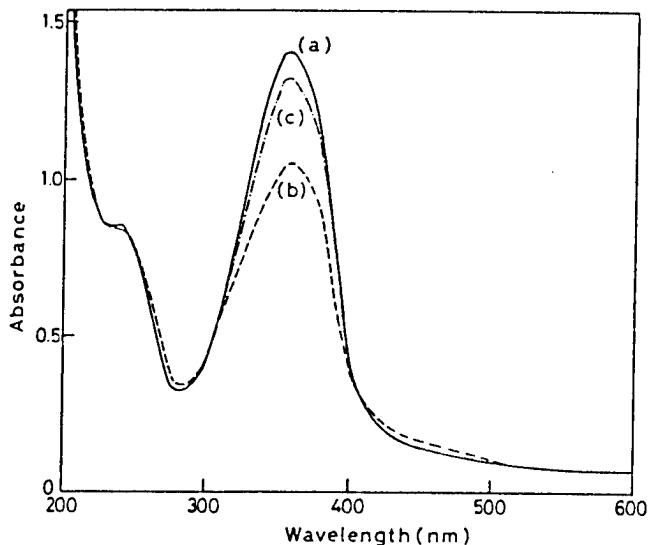


Fig. 1. Absorption spectra of the 60-layered LB film: (a) before irradiation; (b) after irradiation with 365 nm light for 5 min; (c) after irradiation with 436 nm light for 3 min.

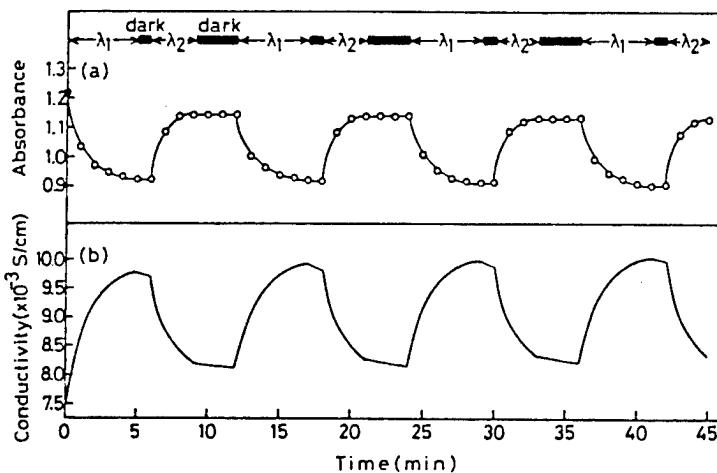


Fig. 2. Changes of (a) absorbance at 356 nm and (b) conductivity of the 60-layered LB film on alternate irradiation with ultraviolet ( $\lambda_1 = 365$  nm) and visible ( $\lambda_2 = 436$  nm) light.

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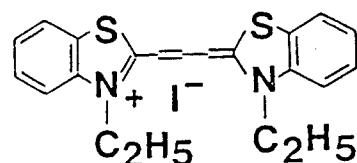
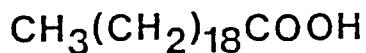
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# IN-PLANE ANISOTROPY OF INTERFACE-ADSORBED COMPLEX LB FILMS

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Interface-adsorbed complex LB films of arachidic acid and a cyanine dye were fabricated using the diffusion-adsorption method, and their optical properties were examined employing a linearly polarized incident.

Figure 1 shows the film-forming materials used. Arachidic acid was dissolved in chloroform and spread on water containing about  $1 \times 10^{-4}$  mol/l of cyanine dye. After the adsorption, the resultant complex monolayer was transferred onto a glass substrate with a width of 13 mm using the vertical dipping technique at a surface pressure of 40 mN/m. If the dipping speed was lower than 10 mm/min, this process yielded good Y-type LB films.



(a) Arachidic acid

(b) Cyanine dye

Fig. 1. Molecular structures of the film-forming materials.

The optical properties of the complex LB films were found to be strongly dependent on the subphase conditions. We have found the condition for obtaining LB films with a large in-plane anisotropy as shown in Fig. 2. The films show both anisotropy of O.D. and that of spectral shape. The transition dipole moment of the red-shifted band is preferentially oriented perpendicular to the dipping direction of the film, while that of the blue-shifted band prefers the dipping direction. These results may be due to the flow orientation,<sup>1,2)</sup> but this type of anisotropic behavior is unique and has not yet come to our knowledge. As for the origin of anisotropy of spectral shape, formation of both H-

like and J-like aggregates, or Davydov splitting of dimers may be considered.<sup>3)</sup> Tentative model based on Davydov splitting will be shown, since it is more suitable.

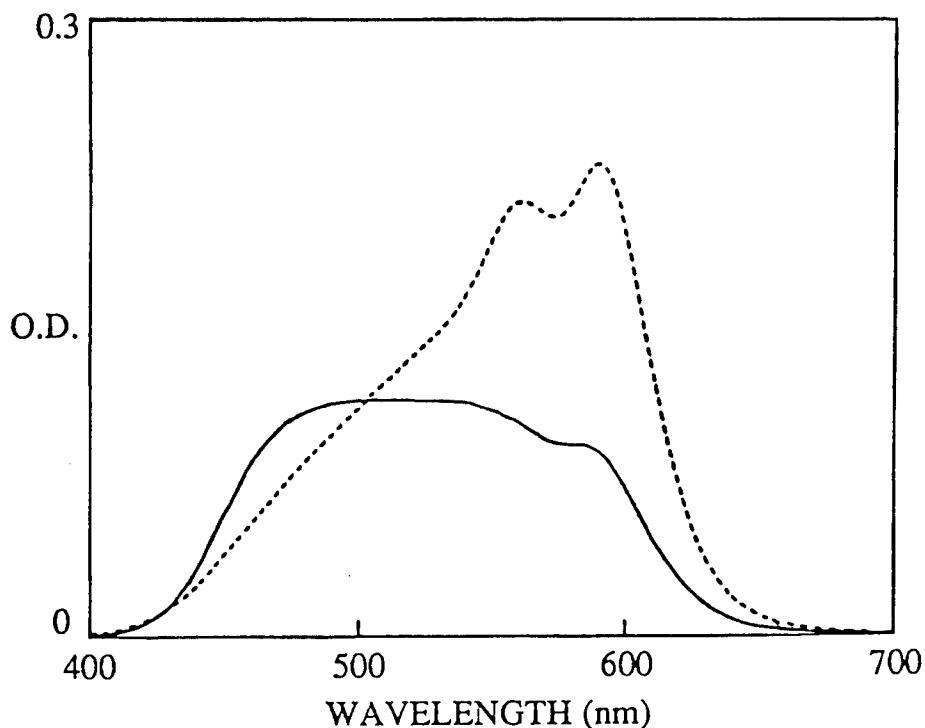


Fig. 2. Absorption spectra of the LB film. The solid and dashed lines refer to the electric vector parallel and perpendicular to the dipping direction, respectively.

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PHOTOINDUCED ELECTROCHROMISM IN MONOLAYER ASSEMBLIES  
OF ION-PAIR CHARGE-TRANSFER COMPLEXES OF  
4,4'-BIPYRIDINIUM IONS

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4,4'-Bipyridinium ion undergoes reversible redox reactions accompanied by marked colour changes (electrochromism) and also forms charge-transfer (CT) complexes as a good electron acceptor with many organic compounds and inorganic anions. Reverse reactions after photoinduced electron transfer via excited CT complexes are usually very rapid and no steady colour changes due to photoreduction of 4,4'-bipyridinium ions had been observed upon excitation of a CT absorption band without employing sacrificial donor anions.

Recently we have reported that excitation of an ion-pair CT complex[1-4] of 4,4'-bipyridinium salts with tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate anion (abbreviated to TFPB<sup>-</sup>)[5] in microcrystals[1] and in organic solutions[4] in vacuo or in Ar resulted in the accumulation of 4,4'-bipyridinium cation radicals which disappeared thermally. The photochemical formation and thermal decay was highly reversible in both systems.[1,4] We now report on photoinduced electrochromism due to electron transfer via excited ion-pair CT complex of 4,4'-bipyridinium ion with TFPB<sup>-</sup> in monolayer assemblies.[6]

A 1:4 mixture of N,N'-dihexadecyl-4,4'-bipyridinium (TFPB<sup>-</sup>)<sub>2</sub> (abbreviated to HV) and arachidic acid (abbreviated to AA) was deposited at 13°C and 20 mN · m<sup>-1</sup> on a quartz plate or on a poly(ethyleneterephthalate) film from an aqueous subphase (pH=6.3). From sharp small-angle X-ray diffraction patterns up to 7th order observed for mixed monolayer assemblies, the spacing of 5.46±0.06 nm was obtained, which coincided with that of cadmium arachidate monolayers. These results indicated that mixed monolayers of HV and AA were

deposited as a well-defined Y-type film. Microcrystals of N,N'-dimethyl-4,4'-bipyridinium (TFPB<sup>-</sup>)<sub>2</sub> salt were prepared on a quartz plate from 1,2-dimethoxyethane solution by evaporating a solvent. These samples were irradiated in vacuo or in Ar using a Hamamatsu 150 W Xe-Hg lamp equipped with an L-39 cut-off filter ( $\lambda > 365$  nm) and a 10 cm water filter to excite their CT absorption band alone.[3]

Upon irradiation the colour of monolayer assemblies changed from pale yellow to blue and the UV/vis spectrum characteristic of 4,4'-bipyridinium cation radical monomer was observed. No indication of dimer formation between 4,4'-bipyridinium cation radicals in monolayer assemblies was found. A broad singlet ESR spectrum ( $g=2.003$ ,  $\Delta H_{m.s.}=14.5$  G) was observed upon irradiation of monolayer assemblies. These results indicated the photoinduced electron transfer from TFPB<sup>-</sup> to 4,4'-bipyridinium ion and also the homogeneous dispersion of HV in a matrix of AA.

Coloured species in mixed monolayer assemblies reversibly decayed and was formed again upon CT excitation as already reported for similar salts in solutions or in microcrystals.[1,4] These reaction cycles were repeated for many times. The decay of coloured species was almost exponential in both (A) monolayer assemblies and (B) microcrystals with similar lifetime ( $\tau_{1/2}$ : (A) 4.3 hr and (B) 4.0 hr). The ESR spectrum of photogenerated 4,4'-bipyridinium cation radicals also showed similar thermal decay. The steady and reversible charge separation between 4,4'-bipyridinium ion and TFPB<sup>-</sup> found in solutions or microcrystals was mainly due to the extraordinary bulk and chemical stability of TFPB<sup>-</sup>.[5] The microenvironment around charge-separated species in mixed monolayer assemblies of HV and AA was deduced to be similar to that in microcrystals from these results.

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Simulation of Primary Process in Photosynthetic Reaction Center  
by Monolayer with Charge Separation Triad and Antenna Molecules

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In the photosynthetic reaction center, solar energies harvested by antenna pigments are funneled to the special pair, which is followed by multistep electron transfer reactions to separate an electron-hole pair far apart across the lipid bilayer thylakoid membrane. The result of these transfers in the organized structure is that reduced products appear on one side of the thylakoid membrane and oxygen appears on the other.

In the present work, we simulated the light harvesting and the following charge separation processes by monolayer molecular assemblies consisting of synthetic antenna pygments and triad molecules. As the antenna pygments, amphiphilic pyrene derivatives were used, whereas the triad molecule was linear and contained a perylene moiety as the sensitizer(S) unit as well as viologen and ferrocene moieties as the electron acceptor(A) and donor(D) units, respectively. In the linear A-S-D triad molecule, the A, S, and D units were linked one another by normal alkyl chains. The antenna pyrene derivatives were fatty acids, which have a pyrene ring (Py) in the middle of the alkyl chains, i.e.  
 $\text{CH}_3-(\text{CH}_2)_n-\text{Py}-(\text{CH}_2)_m-\text{COOH}$  ( $n=9, m=5; n=5, m=9$ ).

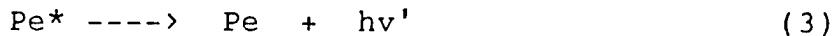
The linear A-S-D triad and the antenna were synthesized by Friedel-Crafts acylation and reduction of the introduced carbonyl groups.<sup>1-3)</sup> Their structural formulae are shown in Fig. 1.

In Fig. 2, the UV and visible absorption and fluorescence spectra of dialkyl pyrene and monoalkylmonoacyl perylene moieties in ethanol are shown. The absorption band for the lowest excited state of the perylene moiety appears in the wavelength region of 400 - 500 nm, whereas the corresponding fluorescence band of the antenna pyrene moiety appears in 370 - 450 nm. The partial overlap of these bands indicates that excitation energies for the pyrene antennas ranging from 300 to 380 nm, where very little

absorption was observed for the perylene moiety, shall be transferred to the perylene moiety in the charge separation unit.

The fluorescence and excitation spectra of the mixed cast film of the triad and the antenna compounds support the following energy transfer and the direct excitation mechanisms.

Energy transfer mechanism:



Direct excitation mechanism:



The photocurrent measurements by the mixed monolayer implies that light harvesting by antenna pigments followed by energy transfer and succeeding charge separation in the reaction center in the photosynthetic primary process could be simulated artificially by monomolecular layer assemblies of the synthetic antenna pigments and triad molecules.

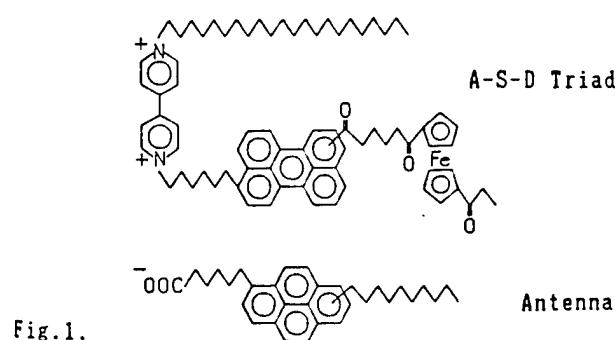


Fig.1.

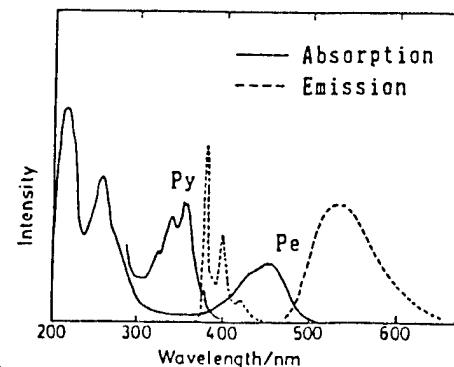


Fig.2.

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# Detections of Adsorption Behavior of Bioactive Compounds to Lipid Membranes by a Piezoelectric Crystal

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Piezoelectric crystals are known to provide very sensitive mass measuring devices because of resonance frequency changes upon the deposition of a given mass on the crystal electrode.

In this paper, we would like to review that the lipid bilayer-coated piezoelectric crystal is useful tool to study the selective interaction of bioactive compounds with lipid bilayers in aqueous solutions.

## 1. Odorants and bitter substances.

Partition coefficients of various bitter and odor substances to lipid bilayers from aqueous phase were obtained from the frequency changes and plotted against the intensity of bitter taste and odor in human. There was a good linear relation with both values, thus, the stronger bitter or odor substances tend to adsorb larger to lipid membranes.

## 2. Anaesthetics

We observed the adsorption behavior of 18 kinds of anaesthetics to lipid-coated piezoelectric crystals both in gaseous and aqueous phases. The results were as follows: (1) there was a good correlation between the potency of anaesthetics and their partition coefficients to lipid bilayers, and (2) anaesthetics adsorbed largely and penetrated into lipid bilayer matrices in the fluid liquid crystalline state and hardly adsorbed onto proteins.

## 3. Surfactant molecules

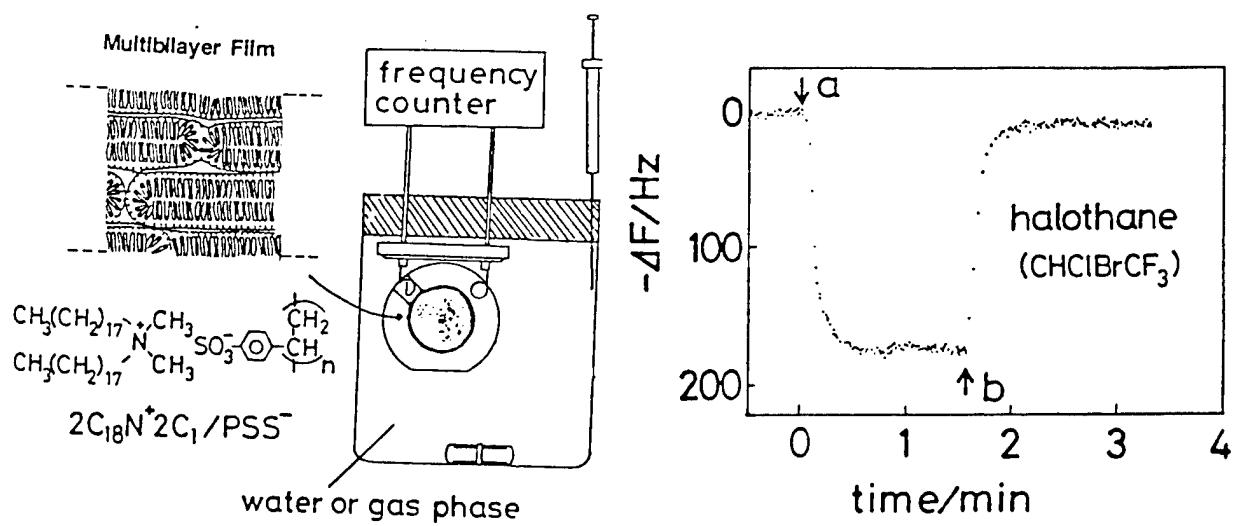
Surfactant molecules are known to irritate lipid membranes due to the adsorption of surfactants or the disruption of lipid matrices. When surfactant molecules were added to lipid-coated piezoelectric crystals in aqueous phases, the frequency decrease

(adsorption of surfactants) and then the frequency increase (solubilization of lipid membranes by surfactants to aqueous solutions) were observed. Surfactants having the higher eye irritancy to cornea lipid membranes showed the larger adsorption to lipid-coated crystals.

#### 4. Antibiotics

The adsorption behaviors of various antibiotics or ionophores to LB films of phospholipids on the crystal were studied in aqueous phases. Polymyxin B, gramicidin S, and duramycin (hydrophobic cyclic polypeptides having a cationic side chain) showed the selective and strong interaction to phosphoethanolamino head groups of LB films ( $2C_{14}PE$ ) and penetrated deeply into phospholipid LB films. When the barrier layers (diacylglycerol) was set in the middle layer of  $2C_{14}PE$  LB films, the penetration of peptides was stopped at the diacylglycerol layers.

In conclusion, the multibilayer film cast or LB film deposited piezoelectric crystals will become a useful tool to detect directly the interaction of bioactive compounds with lipid matrix as a model of biological membranes.



Frequency change of bilayer-coated crystal  
by adsorption of anesthetic(halothane) in water phase

Electrical Properties of Polyimide Langmuir-Blodgett Films Sandwiched between Superconducting Electrodes: Detection of microwaves

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We have examined the electrical properties of ultrathin insulating layers of cadmium arachidate (C20), polyamic acid long alkyl amine salts (PAA) and polyimide (PI), using tunnel junctions with structures of Pb-Bi/PAA(or C20)/Pb-Bi, Au/PI/Pb-Bi and Au/PI/Au. Here, PAA is a precursor to polyimide, and Pb-Bi is a superconducting electrode.

For samples with a structure of Pb-Bi/PAA(or C20)/Pb-Bi, typical I-V characteristics of weak-coupled superconductors are shown in the absence of microwave powers at a temperature below the critical temperature of Pb-Bi superconducting electrodes, when the number of deposited layers are 1, 2 and 3 (Fig. 1). And the normal step structure is shown in the I-V characteristics in the presence of microwave powers with a radiation frequency of 10GHz (Fig. 2). We found that the metallic pathways exist in the LB films. From the solution of the Ginzburg-Landau equations, we obtained the result that the radius of the pathways is smaller than the London-penetration depth of the Pb-Bi alloy. As we can see in Fig. 2, many constant-voltage current steps ruled by the Josephson's frequency condition  $2eV = nh\nu$  ( $n = 1, 2, 3, \dots$ ) are generated. For most of the samples, the steps are generated at the voltages up to about 2mV. Consequently, the efficiency of detecting microwaves is excellent in these samples, although the bridging filaments exist in the LB layers. In the samples with base Pb-Bi electrodes, we could not imidize the PAA LB films into PI LB films, because the base Pb-Bi electrodes are dissolved during the imidization.

For samples with a structure of Au/PI/Pb-Bi, typical I-V characteristics of tunnel junctions are obtained at a temperature of 4.2 K, when the number of deposited LB layers is 27 (Fig. 3). A gap voltage ( $\Delta/e$ ) of about 1.2 mV of the Pb-Bi alloy is seen. The gap voltage depends on the temperature and it approaches zero as the temperature approaches the critical temperature of the Pb-Bi alloy.

For samples with a structure of Au/PI/Au, most of the samples are shorted when the number of deposited LB layers is smaller than 30. On the other hand, typical I-V characteristics of tunnel junctions or insulating layers are obtained when the number of deposited layers is larger than 30.

Finally, we concluded from the experiments described above that the PI LB films become good electrical insulating spacers when the thickness of the deposited layers is more than about 120 Å.

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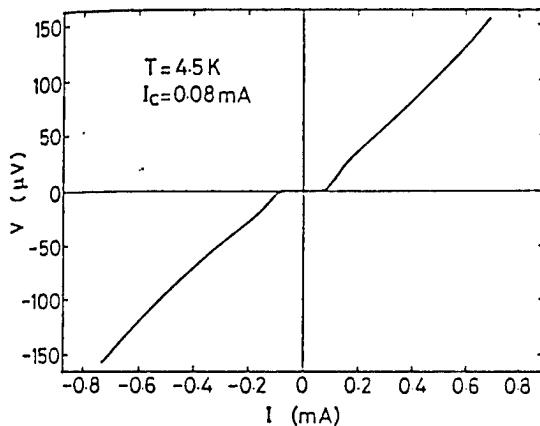


Fig. 1 A typical I-V characteristic for the sample with a structure of Pb-Bi/PAA/Pb-Bi at a temperature of 4.5 K.

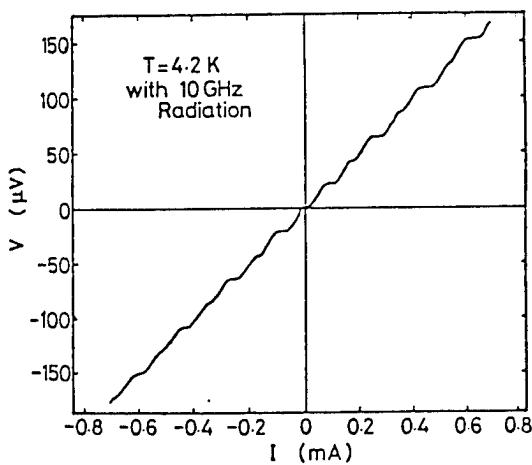


Fig. 2 A typical I-V characteristic for the sample with a structure of Au/C20/Pb-Bi, when microwave power is applied.

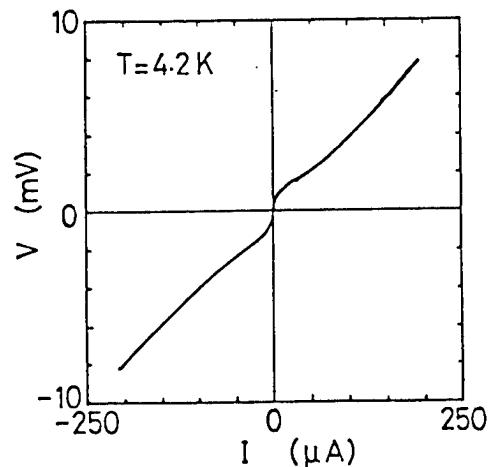


Fig. 3 A typical I-V characteristic for the sample with a structure of Au/PI/Pb-Bi at a temperature of 4.2 K.

# Structural Control of Vacuum-Deposited Thin Films by Use of LB Multilayer

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Physical vapour deposition (PVD) is one of the most widely used techniques to prepare organic thin films. And many efforts to control structures (i.e. molecular orientation, crystal structure, crystalline size and so on) in vacuum-deposited films have been already made by use of various substrates, by controlling the temperature of substrate or by both<sup>1~3</sup>), though the structural control is still major issue toward applications. Here, we report that LB multilayer, when used as a substrate, has big potential for such structural control of long chain molecules. Furthermore, in the process of structural characterization, we have succeeded for the first time in the direct observation of lattice images of monolayers by use of a superconducting cryo-electron microscope.

LB multilayers used as a substrate were deposited onto glass plate using a Lauda film balance. Subphases were aqueous solution of cadmium chloride ( $4 \times 10^{-4}$ M). When an amphiphilic diacetylene of heptacosa-10,12-diynoic acid (14-8C) was vacuum-deposited onto a commercially available glass plate at the substrate temperature (Ts) of 22°C, the film showed the X-ray diffraction patterns of both (00l) and (hkl) reflections : In Fig.1(a), reflections at the 2θ angles lower than 10° are identified to be (00l) and those at higher than 20° to be (hkl), as in the case of PVD films of stearic acid<sup>1</sup>). This result indicates that 14-8C molecules on glass substrate are oriented in the manner both parallel and perpendicular to the substrate, i.e. in mixed orientations. Such mixed orientation was also observed on the glass plate covered with the 10 layers of arachidic acid (C<sub>20</sub>CA)(Fig.1(c)). Elevated temperature, which favorably gives perpendicular orientation for simple fatty acids on the glass plate, did not work for 14-8C on the C<sub>20</sub>CA multilayers (Fig.1(b)). On the contrary, when the glass plate covered with the 10 layers of 14-8C was used as a substrate at the Ts of 22°C, only the (00l) reflections appeared in addition to stronger diffractions of LB multilayers containing cadmium ions (Fig.1(e)),

implying that the merely perpendicular orientation was realized by virtue of molecular orientation controlling power of LB multilayers.

In the case of hydrophobic alkyl diacetylene of octacosa-13,15-diyne, the PVD films on a glass plate was not polymerizable, whereas that on the LB multilayer became highly polymerizable, indicating the clear control of crystal structure of PVD films by LB multilayers.

Electron microscopic observation of these substrates and PVD films, together with the directly observed lattice image of monolayers, will be presented in detail.

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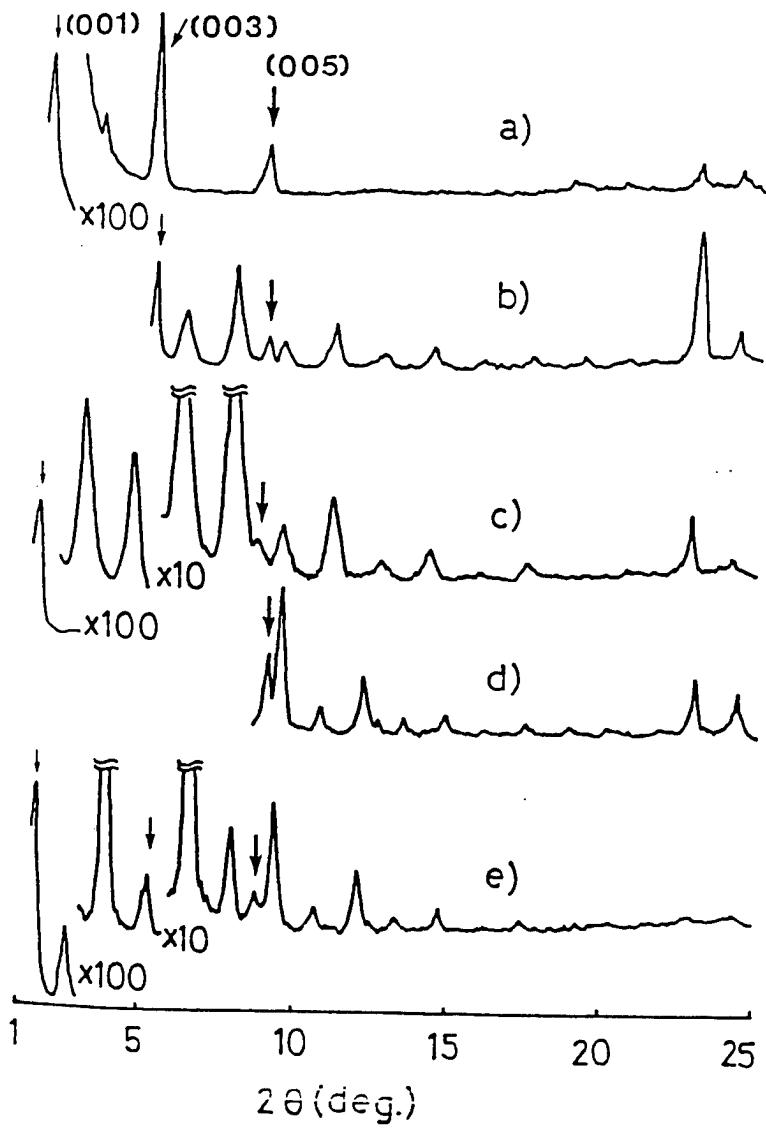


Fig.1. X-ray diffraction patterns of PVD films of 14-8C onto (a) a glass plate at  $T_s$  of  $22^\circ\text{C}$ , (b) LB multilayers of  $\text{C}_{20}\text{CA}$ , (d) 14-8C at  $T_s$  of  $50^\circ\text{C}$  and (c) LB multilayers of  $\text{C}_{20}\text{CA}$ , (e) 14-8C at  $T_s$  of  $22^\circ\text{C}$ .

Two Dimensional Molecular Ordering of Viologen Polymers in  
Langmuir-Blodgett Films

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Design of molecular orientation has attractive attention in many fields of chemistry. Two-dimensional molecular assemblies, such as bilayer membranes and Langmuir-Blodgett films, are suitable matrices for ordered arrangement of guest molecules. Kunitake found that the J-aggregate of anionic cyanine dye was formed on the surface of the cationic bilayer membranes<sup>1</sup>. The J-aggregates of water soluble cyanine dyes were also found at the charged interface of monolayers<sup>2</sup>,<sup>3</sup> and LB films<sup>4</sup>.

Recently we have reported a peculiar odd-even effect on the absorption spectrum of the reduced viologen polymers 1 complexed with anionic bilayer membranes. The odd-even effect was explained in the molecular orientation (Fig. 1).<sup>5</sup> In this paper, we find a similar odd-even effect on surface chemistry of monolayer 2 complexed with viologen polymers and also on electrochemistry of the LB films.

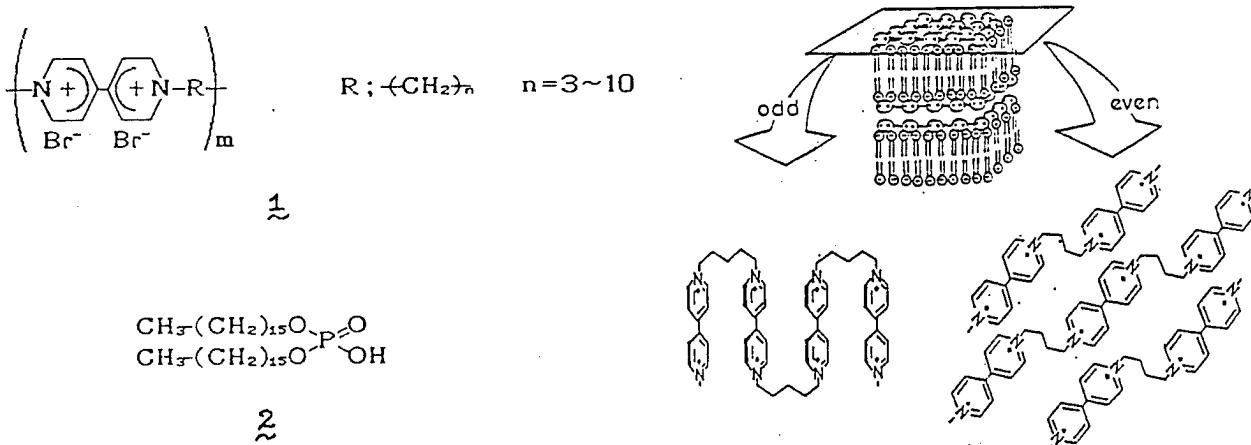


Fig. 1 Molecular orientation of viologen polymer on bilayer membrane

Polyion complex was prepared at the air-water interface when the monolayer of the double-chain anionic amphiphile was spread on an aqueous solution of the viologen polymer (Fig. 2). At lower pressure than 20 mN/m, molecular area increased with increasing the chain length of the viologen polymer. At higher pressure region, so-called liquid condensed and solid phase, a peculiar odd-even effect of the alkyl chain length on the molecular area was found. The area of the odd polymer were smaller than those of the even polymers (Fig. 3).

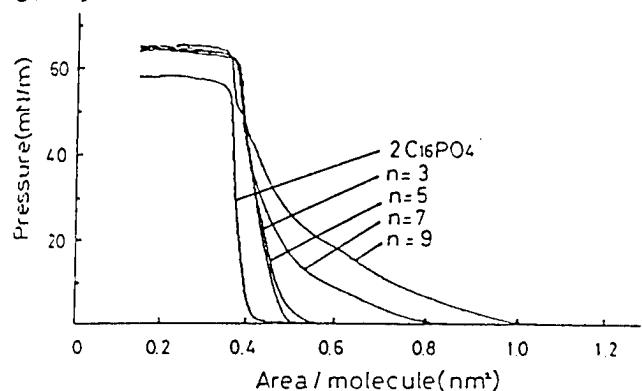


Fig. 2 F-A curves of complex films

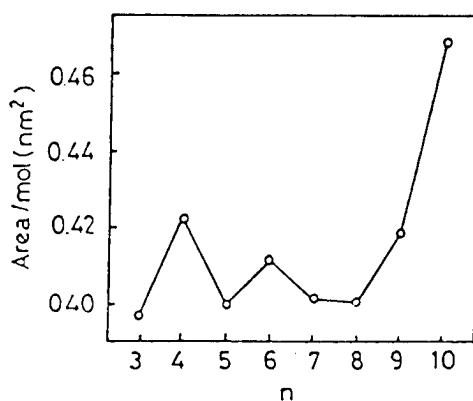


Fig. 3 Mole. area at 45 mNm

The polyion complex monolayer was deposited as a Y-type Langmuire-Blodgett film on an ITO electrode. The LB film modified electrode gave a reversible cyclicvoltammogram due to the redox reaction of the viologen group. The odd-even effect was also found in the redox potential. The peculiar odd-even effect suggests the two-dimensional molecular ordering of the viologen polymer at the regularly ordered charged surface of the anionic monolayer.

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Orientation of Liquid Crystals on Polyimide LB Films:  
Application to Nematic and Ferroelectric EO Devices

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Polyimide (PI) LB films were first successfully prepared by a research group from TIT and Ricoh,<sup>1)</sup> and they were applied to the orientation of nematic liquid crystals. Recently, the PI-LB films were utilized to orient ferroelectric liquid crystals (FLCs) and they were recognized as excellent orientation films to show almost perfect bistability in FLCDs especially in surface stabilized (SS) types.<sup>2,3)</sup> It was also shown that PI-LB films were useful to prepare new LCDs such as STN type.<sup>4)</sup>

This paper will demonstrate the electrooptic (EO) performances of nematic LCDs without accompanying disclinations which were avoided by introducing pretilt angles; and also detailed performances of the SSFLCDs accompanied with the discussion about the mechanisms of the realization of the perfect bistability, coupling strength of LCs with PI-LB films, and molecular conformation of the SSFLCD especially prepared by using PI-LB films. It was shown that the AC conductivity of PI-LB films will take an important role in the appearance of the perfect bistability in the SSFLCDs.

It is also possible to demonstrate a gray scale capability in the memory state by inserting a variable impedance connected in parallel with FLC device with PI-LB films, as shown in figure 1.

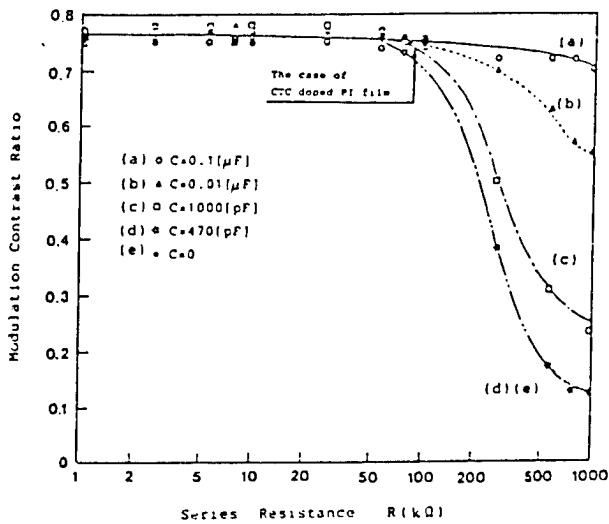


Figure 1. The gray scale capability in the memory state of FLCD with PI-LB films, which is controlled by changing parallel impedance.

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## Molecular Film Technology for Biosensors

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### 1. Introduction

Biosensors generally rely upon the molecular recognition of biological substances for selectivity. A variety of biological substances may be incorporated most commonly in molecular film. Langmuir-Blodgett film technology seems promising in fabricating molecular films for biosensors. There should, however, be so many problems to be solved. One of the technical problems is how to fabricate and stabilize protein molecular films for biosensors. Another problem falls in finding a problem falls in finding a very specific application enough to exaggerate the advantages of the LB film technology over other molecular film technologies. This paper primarily concerns with these problems remained unsolved and the future prospects of molecular film technology for biosensors.

### 2. Protein LB Films for Biosensors

There have proposed several methods for fabricating protein molecular films for use of biosensors. Of these methods the LB film technology seems promising because it is manipulated in an aqueous phase. A protein monolayer spread on the air/water interface, however, is mostly unstable in protein structure and intermolecular arrangement. To stabilize the protein monolayer, the protein structure and intermolecular arrangement. To stabilize the protein monolayer, the protein molecules have successfully been crosslinked at various surface pressures by bifunctional reagents such as glutaraldehyde. The crosslinked protein

monolayer is transferred onto the hydrophobic solid surface.

The crosslinked protein LB film serves as a substrate for depositting monolayers of functional proteins such as enzymes and antibodies.

### 3. Conductive Enzyme Monolayer Films for Biosensors.

A conductive enzyme monolayer film has been synthesized by potential-controlled adsorption of enzyme molecules on the metal surface, which is followed by electrochemical polymerization of pyrrole onto the protein-adsorbed metal surface. The polypyrrole/enzyme film retains enzyme activity and electric conductivity. The enzyme exhibits reversible electron transport through polypyrrole, which leads us to design a new type of enzyme sensor.

### 4. Optical Biosensor for Multi-molecular Information Using Fluorophor-Embedded LB Films

Ultimately thin LB films will find great advantages in fabricating optical biosensors and chemical sensors for multi-molecular information.

The LB film technology has successfully been applied to fabricate an optical biosensor for taste. The principle of sensing is based on fluorophors quenching and enhancing of several fluorescence embedded in the different layers of LB films by taste substances in solution. The sensor responds simultaneously to several types of umami substances such as monosodium glutamate (MSG) and guanyl monophosphate (GMP). Furthermore, cooperative enhancing umami effects of MSG and GMP have first been evaluated by fluorescence enhancing due to coexistence of these substances. An optical biosensor fabricated by LB film technology seems promising in simultaneous recognition of multi molecular information, which will open the gate of simulating taste sensing.

VERTICAL DIPPING METHOD AS A MEANS OF CONTROLLING  
THE IN-PLANE MOLECULAR ORIENTATION  
IN LANGMUIR-BLODGETT FILMS

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In previous papers [1-3], we have presented an analytical model of in-plane anisotropy observed in LB films prepared using the vertical dipping method. The model is an effective medium theory referring to the flow of monolayer during the deposition process. The derivation consists of two stages: (1) evaluation of the velocity potential governing the motion of the monolayer, and (2) examination of the rotatory motion of a particle in this field.

In Stage (1), the monolayer is approximated to be a two-dimensional ideal fluid, and the potential function for a flat substrate is given, e.g., as,

$$W(z) \equiv U + iV = -\left(v_d/\pi\right) \int_{-a/2}^{a/2} \log(z-x') dx', \quad (1)$$

where  $a$  and  $v_d$  are the width of the substrate and the velocity of deposition, respectively.

The friction between the particle and the surrounding medium is taken into account in Stage (2). Using the steady-state approximation, the angular distribution function is written as,

$$P(\theta) \propto \exp\{-(\zeta G/k_B T) \sin^2 \theta\}, \quad (2)$$

where  $\theta$  is the angle between the long axis of the particle and the dipping direction,  $G$  is the eigenvalue of velocity gradient tensor near the substrate, which is given from Eq.(1) as,

$$G = (4/\pi) (v_d/a) (1-4x^2/a^2)^{-1}, \quad (3)$$

and  $\zeta$  is the Bingham-type friction coefficient  $\zeta = \zeta' + \tau_0/G$  assumed allowing for the plasticity of the monolayer [2,3].

The predictions from the model have been experimentally verified in a model system of a merocyanine diluted with a fatty acid.

We have extended this type of analytical approach leading to further predictions for controlling the in-plane anisotropy in LB films. The results will be shown in this report.

Array of substrates

The potential function for an array of flat substrates aligned side by side can be written as,

$$W(z) = -\left(v_d/\pi\right) \int_{-a/2}^{a/2} \log[\sin\{\pi(z-x')/l\}] dx', \quad (4)$$

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where  $l$  is the center-to-center distance between the neighboring substrates. Consequently, we obtain,

$$G = (v_d/l) [\cot\{\pi(x+a/2)/l\} - \cot\{\pi(x-a/2)/l\}], \quad (5)$$

showing the weaker position-dependence than Eq.(3) for finite  $l$  ( $\geq a$ ). The expressions for the face-to-face case are derived by replacing  $\sin$  in Eq.(4) with  $\sinh$ .

#### Removal of the position-dependence

The potential for Miyata's method with a floating barrier [4,5] is obtained if we put  $l=a$ , i.e.,

$$W(z) = iv_d z, \quad (6)$$

which results in  $G=0$ , indicating that the flow orientation effect ceases to exist in this case.

Another interesting case may be the use of a cylindrical substrate with a radius  $\rho$ , which is represented by,

$$W(z) = -v_d \rho \log z, \quad (7)$$

resulting in  $G=v_d/\rho$  everywhere at the substrate.

#### Asymmetric deposition

The cases dealt with so far refer to the normal deposition with the value of transfer ratio  $r$  being unity almost everywhere at the substrate. Asymmetry in  $r$  between the front and the rear can be expressed if we introduce a function,

$$W(z) = i(v_d/\pi) \int_{-a/2}^{a/2} \{(a^2/4-x'^2)^{1/2}/(z-x')\} dx', \quad (8)$$

which corresponds to the case that the monolayer is normally deposited on the front but peeled off from the rear ( $r=1$  for  $y>0$  and  $r=-1$  for  $y<0$ ), where  $G$  is given as,

$$G = 2(v_d/a)(1-4x^2/a^2)^{-3/2}, \quad (9)$$

showing the stronger position-dependence than Eq.(3).

Linear combinations of Eqs.(1) and (8) can express more realistic cases, e.g., the arithmetic average of the both refers to the case with complete slipping of the monolayer at the rear.

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FABRICATION OF COPOLY(METHACRYLIC ACID - METHYLACRYLATE) L-B FILMS USING L-B TROUGH OF MOVING WALL TYPE

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Ordinary Langmuir-Blogett(L-B) trough, whose width is much wider than that of the solid substrate, has two major problems during the film deposition process as follows;

- (1) The monolayer is unhomogeneously compressed because of friction between monolayer edges and trough.
- (2) The monolayer flows with shears from all sides of the trough to the solid substrate to fill a hole developed during the deposition. Therefore, the L-B films deposited on the solid substrate may have a different molecular orientation from that of a compressed monolayer[1,2].

In order to improve these defects, we have constructed a new L-B trough as shown in Figure 1[3]. Two poly(tetrafluoroethylene) tapes(moving walls) are connected with both edges of the barrier, and the width is the same as that of the solid substrate to prevent the shear flow of the monolayer during the deposition. Since the monolayer moves together with the moving walls, there is no friction between monolayer edges and walls. Therefore, it is easy to deposit the rigid or viscous monolayer such as polymer monolayers.

On the other hand, polymer L-B films have attracted much attention because they are expected to improve the mechanical strength and thermal stability of low molecular weight L-B films[4,5]. However, it is very difficult to deposit successively a polymer monolayer on the solid substrate as ordered multilayers, even if it forms a condensed phase, because the polymer is too viscous to follow the deposition by means of ordinary L-B trough.

We have found that the successive deposition of polymer monolayer could be done by this new deposition system. In this report, we describe the nature of methacrylic acid - methylacrylate(1:1mol%) random copolymer(P(MAA-MA)) monolayer and its L-B films. This compound was kindly supplied by Nippon Oil and Fats Co. Ltd., Japan.

Figure 2 shows the  $\pi$ -A isotherms of the monolayer of P(MAA-MA) on pure water(curve 1), and on subphase containing either cadmium ions(curve 2) or lanthanum ions(curve 3-6) at various pHs. On pure water, the monolayer is unstable and never forms the solid phase. In the case of cadmium ions  $\pi$ -A curve indicates the collapsed monolayer. On the contrary, the monolayers on the subphase containing lanthanum ions have exhibited the typical  $\pi$ -A curves defining the solid phase. The cross-sectional area per unit, when extrapolated to  $\pi=0$  at pH6.89, is about  $22.9\text{A}^2$ .

By using this new deposition system, P(MAA-MA) monolayer cross-linked by lanthanum ions was deposited on a hydrophilic glass substrate as Z-type film. This multilayer assembly film gave a clear X-ray diffraction pattern showing a layer spacing of  $8.43\text{A}$ . From these results, we are speculating following

structure, where MAA segments submerge in the subphase and MA segments are out of the subphase just on MAA segments.

Since P(MAA-MA) monolayer is two-dimensionally cross-linked by lanthanum ions on the air-water interface, its multilayer assembly film is expected to be thermostable, high-strength and high-modulus.

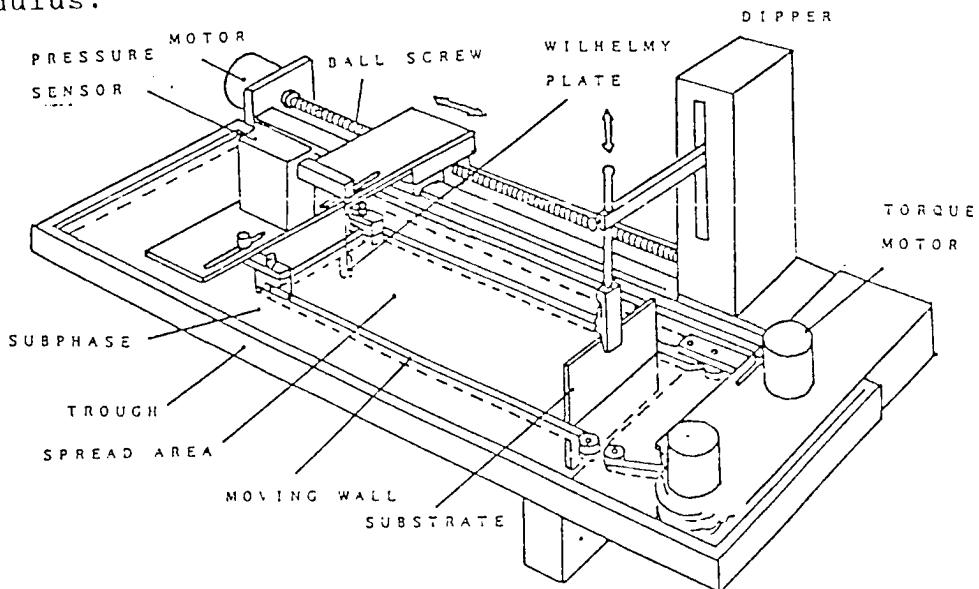


Fig.1 Schematic diagram of the moving wall type L-B trough

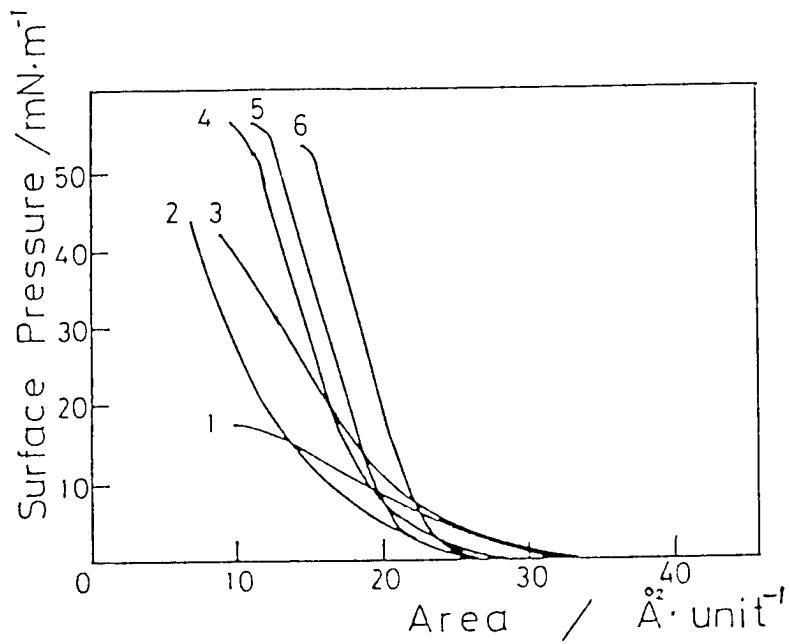


Fig.2  $\pi$ -A isotherms of P(MAA-MA) monolayers  
 (1) pure water, (2)  $\text{Cd}^{2+}$ ; pH 7.07, (3)  $\text{La}^{3+}$ ; pH 5.10  
 (4)  $\text{La}^{3+}$ ; pH 6.05, (5)  $\text{La}^{3+}$ ; pH 6.40, (5)  $\text{La}^{3+}$ ; pH 6.89

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DESIGNING OF A NEW L-B TROUGH WITH ZONE HEATING MECHANISM  
ABOVE THE WATER SURFACE

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In the L-B technique, monolayer at the air-water interface is deposited onto a solid substrate such as a glass slide. The thickness of L-B film is controlled by the number of deposition times. The method of controlling the numbers of the layer of L-B films has not been improved during past 50 years. However, there are two drawbacks for this method to prepare thick films. One is that it takes longer time which is not efficient and also introduction of dusts during deposition. Other is disadvantageous that some defects or cleavages may grow with the times of deposition. Therefore it is often said that the quality of thick L-B films is not up to the expectation. Recently, we have found that an ordered multilayer was formed on the subphase by the zone-heat treatment of monolayer and the thickness of the multilayer can be controlled both by the surface pressure and applied temperature. In this paper, we describe the efficiency of zone-heat technique and also the ordered structure of multilayer by X-ray diffraction.

We designed the zone-heat mechanism above the moving wall type L-B trough as shown in Fig.1. The zone-heater can heat the monolayer on the subphase within 1 mm and move slowly both towards the substrate and the barrier. This heater is able to raise the temperature of the water surface up to 75 °C when a power of 110 W is applied.

To investigate zone-heat mechanism, the stearic acid monolayer was prepared on the subphase containing cadmium ion at pH 6.6. After compressing the cadmium stearate monolayer to 30 mN/m, the zone-heater with a power of 110 W was moved by 5 mm/min. at 1 mm above the monolayer. At a constant pressure, a decrease in the surface area was observed in proportion to moving distance of the zone-heater as shown in Figure 2. This suggests that the surface pressure decrease by zone-heat treatment. Then the compressed film was transferred to the substrate only one time. Figure 3 shows the X-ray diffraction pattern of this film and 5 layers of L-B film deposited by the ordinary L-B technique. The diffraction pattern of this film shows clear peaks up to a (007) refraction. To our surprise, the zone-heat treated film has a layer spacing of 5.1 nm. Furthermore, the X-ray intensity of this film was almost same as that of 5 layers. This indicates that the Y-type multilayer (5 layers) was made on the subphase by using zone-heat treatment. The number of layers on

the water surface depends both on the surface pressure and applied temperature. When the pressure decreases from 30 mN/m to 20 mN/m at the same applied temperature, the number of layer changes from 5 to 3. Since X-ray diffraction pattern of the zone-heat treated film becomes sharper or the half width is much narrower, the multilayer structure obtained by this technique is much ordered than those prepared by the ordinary technique.

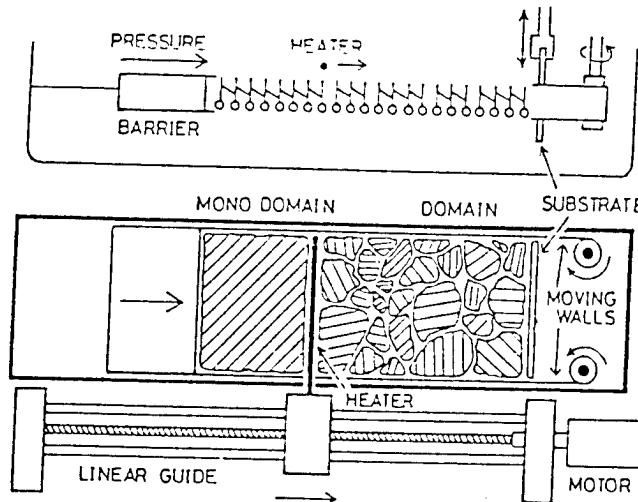


Fig.1. A design of a new LB trough with zone-heat mechanism.

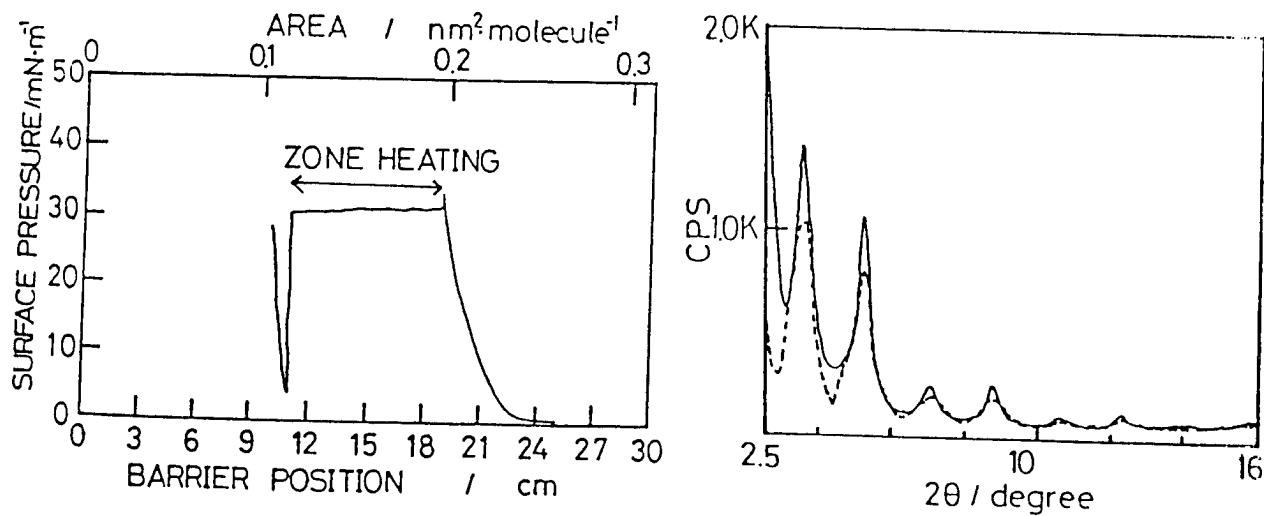


Fig.2. Pressure-area curve of cadmium stearate during zone-heat treatment, when applied temperature is 75 °C.

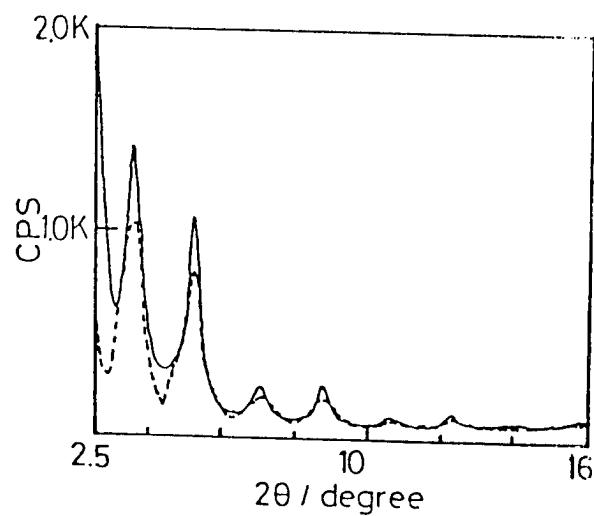


Fig.3. X-ray diffraction pattern of treated film (solid line), and 5 layers of LB film deposited by an ordinary technique (broken line).

LB films of Long-chain Derivatives of Amino acid  
containing Aromatic rings

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Previously, we investigated the control for molecular orientation of amphiphilic dyes and also for polymerizability of amphiphilic amino acids in the LB films. In this work, with long-chain derivatives of amino acids containing aromatic rings such as naphthalene and pyrene (Fig.1) we have examined the arrangement of  $\pi$ -electron

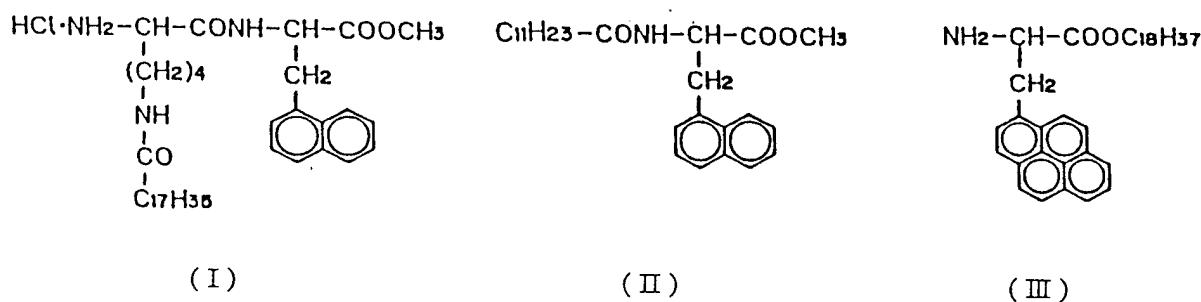


Fig.1

system in the LB films by circular dichroism together with UV absorption and fluorescence spectra.

Fig.2 shows the surface pressure-area isotherms for monolayers of long-chain derivatives of lysinyl-naphthylalanine(I) and naphthylalanine(II). In the former, a transition region from the expanded to condensed state appears at the molecular area of  $50\text{-}60\text{\AA}^2$  and about  $25\text{mN/m}$ . While the UV absorption spectra for the monolayer(I) on water were almost similar to the solution spectrum irrespective of the surface pressure, those for the LB films exhibited a slight red shift of  ${}^1\text{B}_\text{b}$  ( $224\text{nm}$ ) and  ${}^1\text{L}_\text{a}$  ( $282\text{nm}$ ) bands due

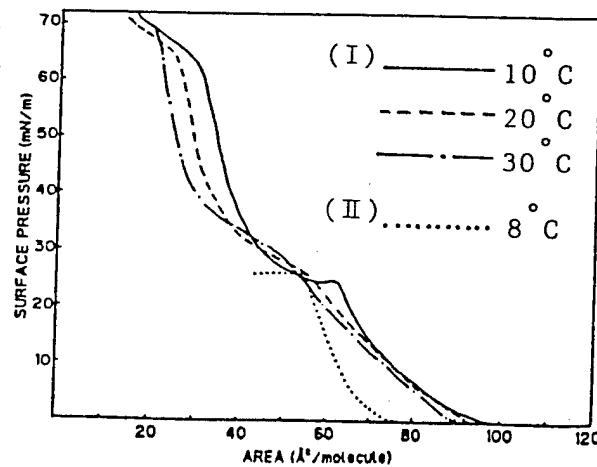
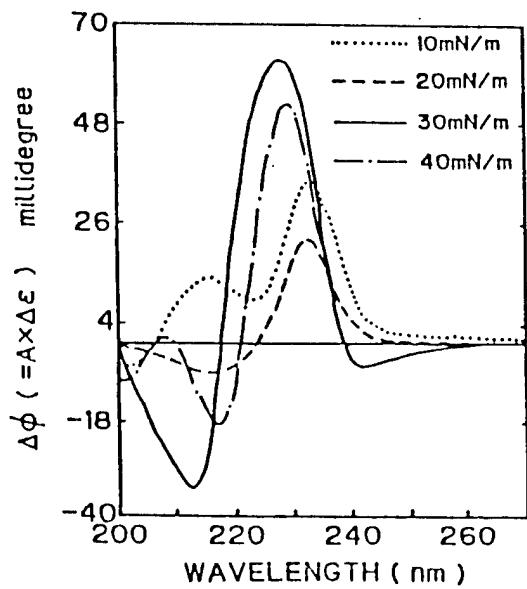


Fig.2.  $\pi$ -A isotherms of (I) and (II)

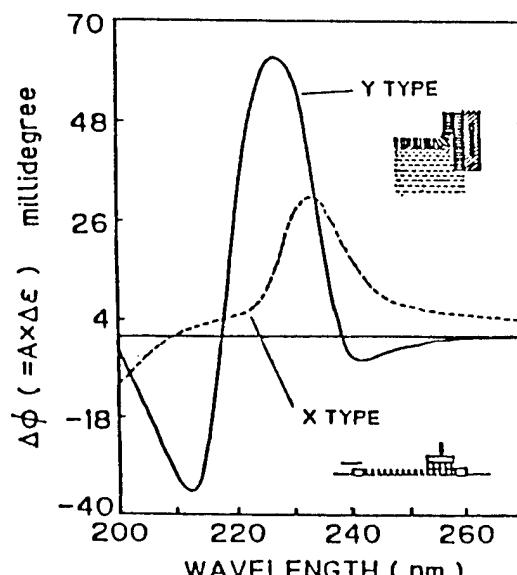
to naphthalene, in comparison with the solution spectrum. In the fluorescence spectra of the LB films, a small excimer emission was observed in addition to the monomer emission.

Circular dichroism (CD) of the LB films was measured by rotating the sample plate about the polarized light to remove the influence of linear dichroism. As shown in Fig.3, it has been found that the CD spectra of LB films of lysinyl-naphthylalanine derivative(I) change significantly with surface pressures on deposition. Particularly, the Y-type LB film prepared at 30mN/m higher than transition pressure exhibits a strong Cotton effect due to the interaction of the  ${}^1B_b$  transition moment of naphthalene. The X-type multilayers prepared by horizontal lifting method showed weaker Cotton effects as compared with the conventional LB films. Therefore, the above Cotton effect is considered to be ascribed to the strong interlayer interaction of the  $\pi$ -electron system in addition to the intralayer interaction. On the other hand, the CD spectra for LB films of lauroyl derivative of naphthylalanine(II) were only slightly dependent on surface pressures.

If polycondensation can be achieved in the mono- and multilayer of these long-chain derivatives of amino acids containing polycyclic aromatic rings, fascinating thin films of polypeptides which may be interesting for light-harvesting and energy or electron transfer system.



(a) Effect of surface pressures



(b) Effect of deposition types

X-type:Horizontal lifting method  
at 33.5mN/m  
Y-type:Vertical dipping (LB)  
method at 30.0mN/m

# Langmuir-Blodgett Films of Octa-alkyl Phthalocyanines

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Various substituted phthalocyanine (Pc) derivatives studied previously for L-B films have ether or ester linkages between the macrocycle and alkyl groups. In this work, Pc derivatives (Insert in Fig.1) attached directly with eight alkyl chains such as octyl, decyl and dodecyl groups were newly synthesized. Figure 1 shows the surface pressure - area isotherms for the monolayers of  $(C_8H_{17})_8Pc$ ,  $(C_{10}H_{21})_8Pc$  and  $(C_{12}H_{25})_8Pc$ , spread from the toluene solution. Surface pressures begin to develop at the molecular areas of  $130 - 160 \text{ } \text{\AA}^2$  and the films become very rigid at the areas in the range of  $70 - 100 \text{ } \text{\AA}^2$ . Values of the limiting area ( $A_{\pi \rightarrow 0}$ ) fall into the range of  $80 - 110 \text{ } \text{\AA}^2/\text{molecule}$ . It is considered that the Pc macrocycles tend to lie nearly flat on the surface, at least in the region of lower pressure. However, in the case of monolayers spread from the chloroform solution the apparent molecular areas were very small as about  $40 \text{ } \text{\AA}^2$ , which seems to be due to any aggregates formation in the films.

The monolayers spread from the toluene solution can be deposited on solid supports by the horizontal lifting method. The optically measured film thickness for the X-type multilayers prepared at  $18.8 \text{ mN/m}$

is plotted against the

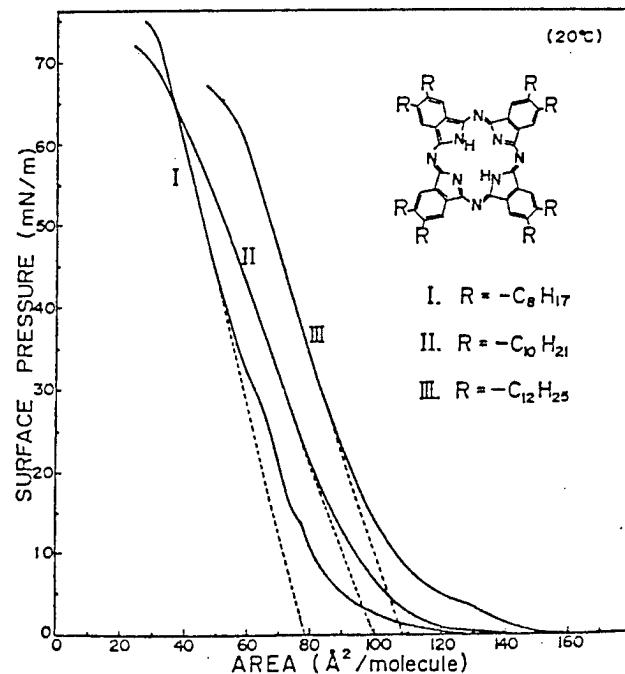


Fig.1. Surface pressure - area isotherms of octaalkyl phthalocyanines.

number of layers, as shown in Fig. 2. The values of thickness per layer are 10.8 Å, 12.1 Å and 15.2 Å for  $(C_8H_{17})_8Pc$ ,  $(C_{10}H_{21})_8Pc$  and  $(C_{12}H_{25})_8Pc$ , respectively.

Figure 3 shows the polarized visible absorption spectra for the multilayer of  $(C_{10}H_{21})_8Pc$  in comparison with the solution spectrum, in which the 350 nm band shifts toward the 340 nm and is relatively enhanced, whereas the strong bands at 670 and 705 nm are spread and broadened at 614 and 774 nm in the film. The results of polarized spectra at 45° incidence for the multilayers together with the film thickness indicate the molecular orientation of Pc macrocycles rather parallel to the surface.

Polarized infrared spectra for the multilayers have also supported the nearly parallel orientation of Pc and the vertical orientation of hydrocarbon chains.

Furthermore, these Pc multilayers on ITO electrodes exhibited electrochromism in the aqueous KCl cell. When a positive voltage was applied to the film through the electrode (oxidation), the original peaks at 614 and 774 nm were shifted to 605 and 760 nm and the absorbances decreased. The reversible color change was observed by reduction of the film.

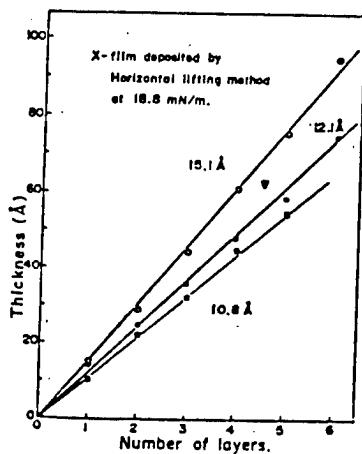


Fig. 2. Thickness of PC multilayers vs. number of layers.

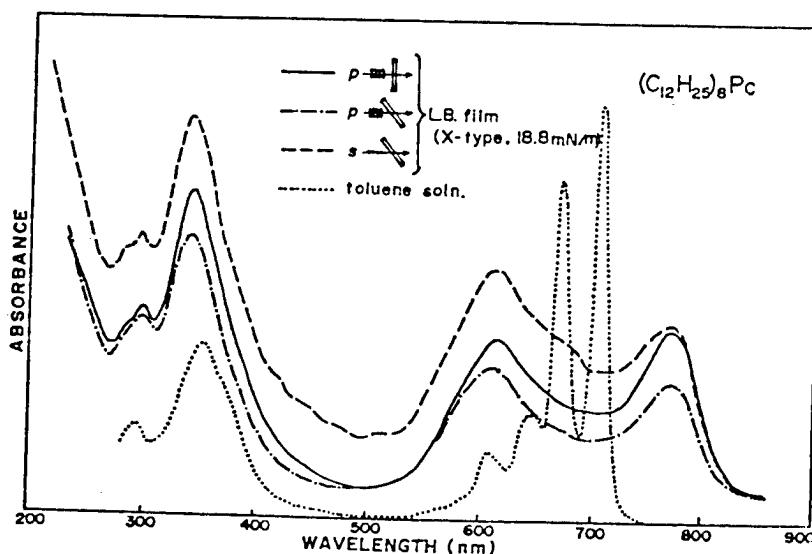


Fig. 3. Polarized electronic spectra of  $(C_{12}H_{25})_8Pc$  film as compared with the solution spectrum.

MONOLAYERS AND LANGMUIR-BLODGETT FILMS OF AMPHIPHILIC CYANINE  
DYE WITH MESOGENIC UNIT IN THE HYDROPHOBIC PART.  
EFFECT OF MATRIX MOLECULES

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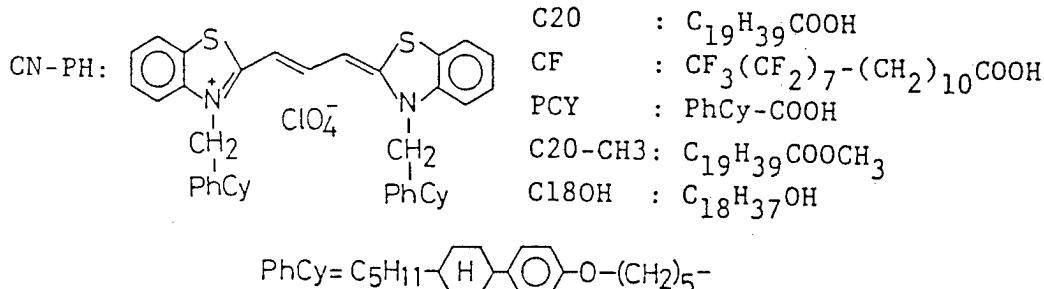
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Langmuir-Blodgett (LB) technique has been considered as one of the most promising candidates for preparing organic thin films with functional parts in regular arrangements. For a typical film-forming molecule, the intermolecular interaction between the hydrophobic parts can be enhanced by introducing a mesogenic unit into the hydrophobic part, which offers the possibilities of controlling functions of the resultant LB films.

We have reported that large in-plane spectral anisotropy was observed for the mixed LB films of CN-PH with C20<sup>1,2</sup>, which was explained referring to the two extreme models of the flow orientation of the crystallites at the air-water interface during the deposition process: the continuum model<sup>3,4</sup> and the 'channel-and-iceberg' model<sup>2</sup>.

The deposition of the mixed monolayers of CN-PH with a matrix was carried out at 25 mN m<sup>-1</sup> at 290 K using the vertical dipping method. The dipping speed was varied from 5 to 100 mm(min)<sup>-1</sup>.



Excess free energy of mixing,  $\Delta G_{xs}^{\pi}$ , reflects the degree of the intermolecular interaction between the two components and the miscibility with each other. This value is graphically obtained from  $\pi$ -A isotherms. It seems from the values of  $\Delta G_{xs}^{25}$  that the miscibility with CN-PH increases in the order: C20 < CF < PCY.

In-plane anisotropy was obtained from the peak heights as  $A_{\parallel}/A_{\perp}$  ( $A_{\parallel}$  and  $A_{\perp}$  are the peak absorbances when the polarization of light is parallel and perpendicular to the dipping direction, respectively) when  $A_{\parallel} \geq A_{\perp}$  and  $A_{\perp}/A_{\parallel}$  when  $A_{\parallel} < A_{\perp}$ . It is clearly seen in Fig. 1 that this value is significantly larger than unity when  $\Delta G_{xs}^{25} \geq 0$  and that it tends to be around unity when  $\Delta G_{xs}^{25} < 0$ . This phenomena suggest that the components with lower miscibility tend to form crystallites at the air-water interface and to show in-plane anisotropy.

Two extreme models are proposed for the flow orientation of the crystallites at the air-water interface during the deposition process as shown in Fig. 2. The first one is the continuum model in which the velocity potential can be defined for the motion of

the monolayer. The orientation of a crystallite of elongated shape is governed by the velocity gradient and the Brownian motion during the deposition process, and the long axis of the crystallite is preferentially oriented along the dipping direction. The other model is the 'channel-and-iceberg' model. The velocity potential cannot be defined in this case. Icebergs represent the component which moves less quickly and hence whose density on a solid substrate is smaller than the rest of the monolayer until the dipping speed reaches a certain critical value. But when the dipping speed exceeds the critical value, the monolayer comes to be described by the continuum model.

To ascertain which of the two models is applicable to a given system, we obtain the ratio  $R$  of the absorbance at a peak position at the dipping speed  $5 \text{ mm(min)}^{-1}$  to that at the dipping speed  $100 \text{ mm(min)}^{-1}$  of unpolarized spectrum. It seems that there is no apparent relationship between the value of  $R$  and  $\Delta G_{xs}^{25}$ . That is, the excess free energy of mixing has little to do with the rheological behaviors of the crystallites formed in the monolayer.

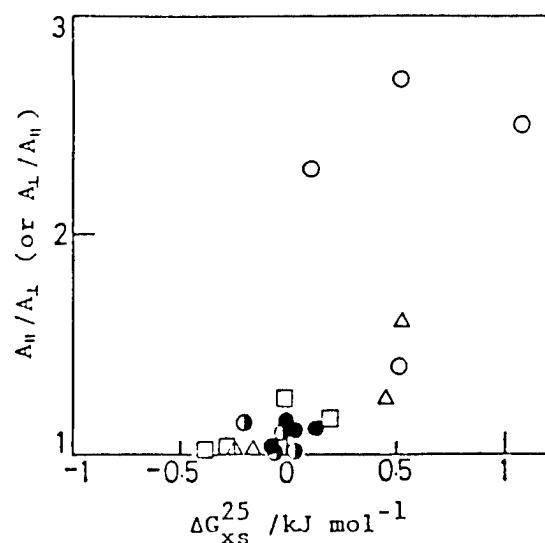


Fig. 1 In-plane spectral anisotropy as a function of excess free energy of mixing: C2O( $\circ$ ), CF( $\triangle$ ), PCY( $\square$ ), C2O-CH<sub>3</sub>( $\bullet$ ), Cl<sub>8</sub>OH( $\bullet$ ).

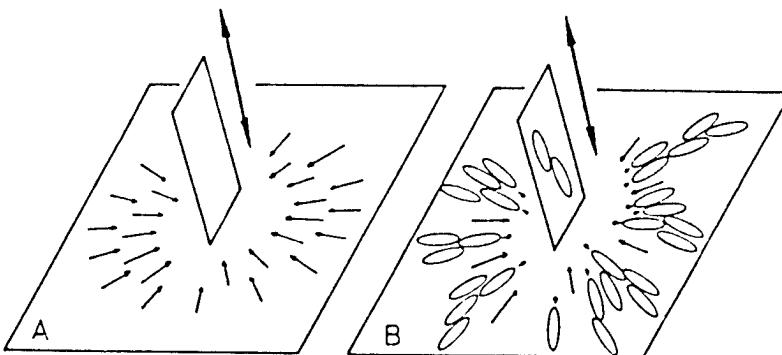


Fig. 2 Schematic view of the deposition process: the continuum model (A) and the 'channel-and-iceberg' model (B). Ellipses shown in B represent 'icebergs' which move less quickly than the rest of the monolayer until the dipping speed reaches a certain critical value.

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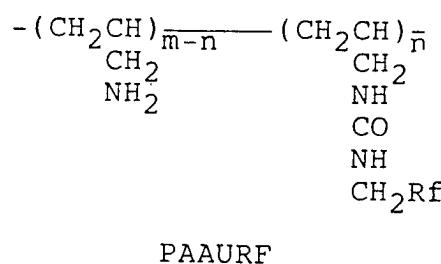
Langmuir-Blodgett Films of Polyallylamine Modified with Long Perfluoroalkyl Chains by Urea Bonds

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Long perfluoroalkyl (Rf) chains on the surface show excellent properties as water- and oil-repellency, low friction, oxygen affinity, etc. Consequently Langmuir-Blodgett (LB) films of polymer containing Rf chains are expected as functional thin films which possess excellent surface properties because of highly oriented ordering of Rf chains. We have reported LB films of polyallylamine modified with Rf chains by amide bonds<sup>1)</sup> and thermal cross linking of the LB films.<sup>2)</sup> Here we wish to report LB films of new polymers modified with Rf chains by urea bond, which is more stable against hydrolysis than amide bond, and thermal cross linking of the polymer LB films.

The new polymers (PAAURF) were synthesized by the reaction between polyallylamine (PAA ; Mw = 5200 - 6700) and 1,1-dihydroperfluorononyl isocyanate. The modification ratio to amino groups in PAA could be controlled by the added amount of the isocyanate, and the various modified polymers (PAAURF12 - 58) were prepared.



$$m \approx 100$$
$$\text{Rf} = -\text{CF}_2(\text{CF}_2)_6\text{CF}_3$$

n/m	PAAURF
0.12	PAAURF12
0.16	PAAURF16
0.24	PAAURF24
0.58	PAAURF58

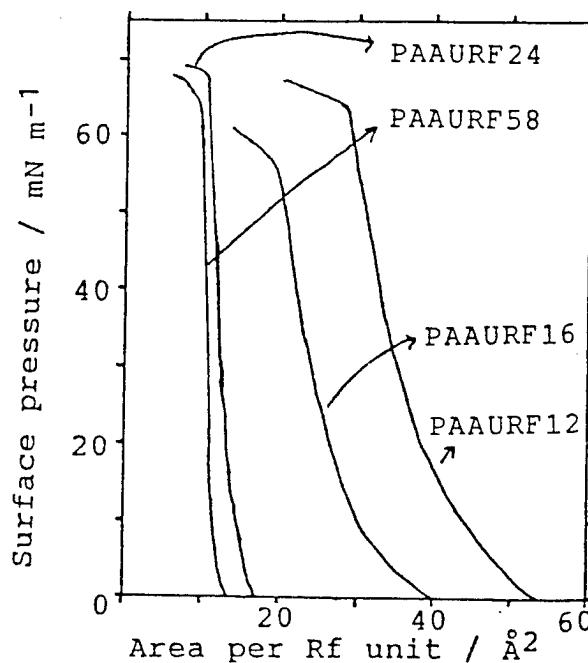


Fig. 1. F-A isotherms of PAAURF.

Figure 1 shows the surface pressure - area (F-A) isotherms for the monolayers of PAAURF at 290 k. The monolayers of PAAURF were spread from the benzene / trifluoroethanol solution on the water surface. The  $\bar{A}_0$  value of highly modified polymers PAAURF24 and PAAURF58 were lower than the section area of  $CF_2$  chain (28 Å), which shows that Rf chains are put on one upon another.

The surface monolayers of PAAURF were deposited on the slide glasses, and critical surface tension calculated from the contact angles of n-alkanes on the films and monolayer's thickness of the films were measured. Characterization of the LB films indicated that the highly modified polymer shows thick monolayer.

Thermogravimetry (TG) of PAAURF powder was carried out and its differential (DTG) curves are shown in Figure 2. Several types decompositions are observed in DTG curves. In the previous paper<sup>2)</sup>, the decomposition at ca. 440°C has been proven to indicate the thermal cross linking of the polymer. This type decomposition (dec.A) is observed in DTG curves of PAAURF, and this suggest that thermal cross linking of PAAURF proceeds.

The LB films of PAAURF were dipped into trifluoroethanol. Characterization of the films showed that critical surface tension was not changed by dipping into trifluoroethanol if the LB films were heated. This result indicated that thermal cross linking occurred in the LB films.

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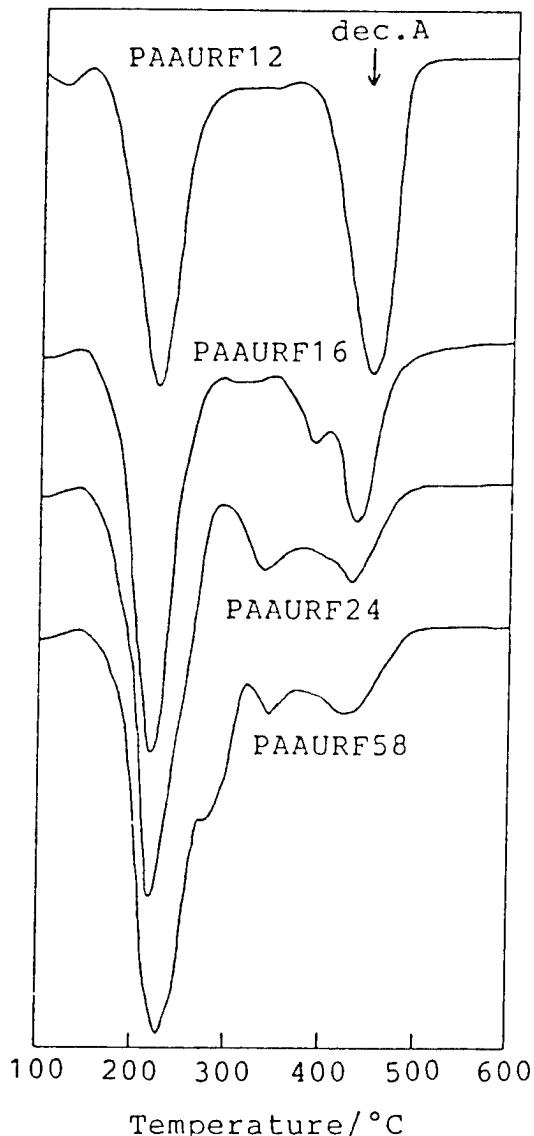


Fig.2 DTG curves  
of PAAURF powder in  $N_2$

Preparation of Langmuir-Blodgett films of long chain  
alkylammonium salts

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Since the cationic monolayer such as long chain alkylammonium salts forms liquid-expanded film on distilled water, the cationic monolayer is difficult to deposit onto substrate in multilayer form. Therefore, Kunitake et al.<sup>1</sup> have reported on the preparation of the LB film for alkylammonium salt by adding polyanion into the subphase.

In the present work, we have studied another possibility of preparation on the LB film of the following alkylammonium salts having mono-, di-, and trialkylchains without using any polyanions in subphase;



The deposition of monolayer on slide glass was performed by using the Kuhn type apparatus. The formation of the LB film for these salts was confirmed by means of IR-ATR, XPS, and X-ray diffraction measurements. The stability of the LB films was examined by the contact angle measurement.

For I and I', the preparation of LB film was tried at various conditions of pH, surface pressure, temperature, and concentration of some heavy metal salts in the subphase. The uniformly deposited film, however, was not formed in the appraisable quality. For II and III, the deposited films were possible to transfer in multilayer form from plain water surface only at the surface pressure which is equal to or slightly more than the ESP for each salt.

Figure 1 shows the plot of number of times for deposition against the IR absorbance of the  $CH_2$  stretching vibration band at  $2920\text{cm}^{-1}$  for the films formed on ZnSe prism. The deposited films of II and III salts are considered to be piled up regularly on slide glass as be expected from the results for cadmium stearate LB film. This finding was also supported

from the result of the XPS analysis. Eventually, it is concluded that the LB films formed with II and III take the molecular arrangement of the X-type from the following two aspects; (1) the slope of the II or III curve in Fig. 1 is just half that of cadmium stearate LB film. (2) X-ray diffraction pattern of the III film gives the layer-to-layer distance of 30.0 Å which is very close to the extended size of the III molecule.

Figure 2 shows the time dependence of the contact angle measured with water put on each ninelayer film of III and cadmium stearate. It was observed that the contact angle of III film gradually decreases with time, compared to that of cadmium stearate film. The result suggests that when the III film touches with water it becomes less stable because of the reorientation of molecules in the outer layer or the penetration of water into the inner layer through hydrocarbon chains.

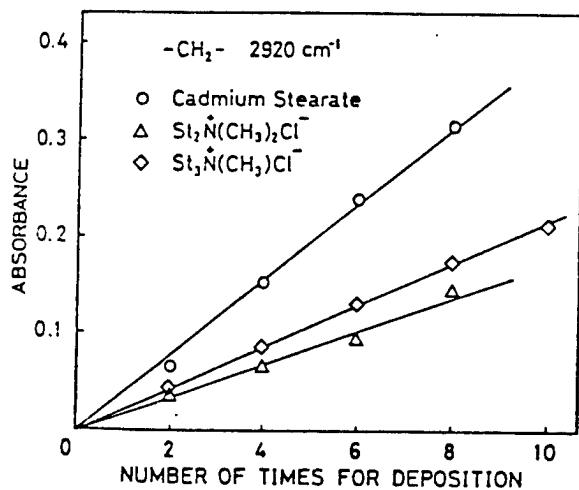


Fig. 1. Absorbance vs number of times for deposition.

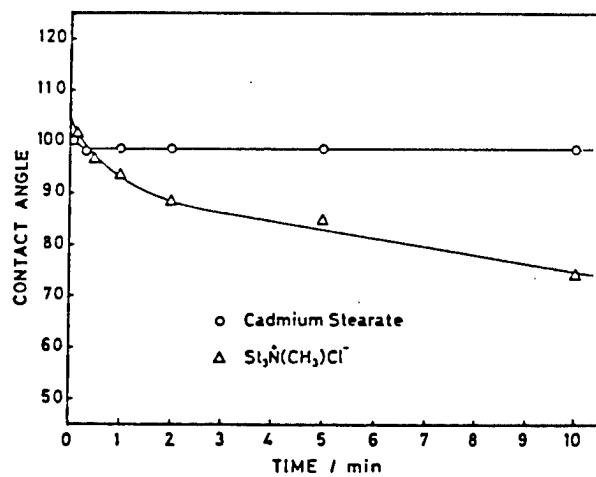


Fig. 2. Time dependence of the contact angle.

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Studies on Langmuir-Blodgett films fabricated from the mixed monolayers  
containing polydiacetylene and polythiophene derivatives

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### 1. INTRODUCTION

$\pi$ -Conjugated polymers have received much attention because they are promising materials for future optical and microelectronic devices. The relationship between their structure and functions have been intensively studied especially using LB films. It has been newly found that stable mixed monolayers containing amphiphilic diacetylene derivative [pentacosa-10,12-dynoic acid] (DA) and poly(3-hexylthiophene) (PHT) can be formed on an aqueous subphase. The structure of the LB films, which were fabricated from the mixed monolayers, has been investigated by X-ray diffraction, FT-IR, secondary harmonic generation (SHG) and so forth.

### 2. EXPERIMENTAL

Commercially available DA was used without further purification. PHT was prepared by chemical polymerization with  $\text{FeCl}_3$ . Monolayers were spread from chloroform solutions of the mixture of DA and PHT on a purified aqueous subphase containing  $3 \times 10^{-4}$  M  $\text{CdCl}_2$ . The LB films were fabricated from the mixed monolayers by an usual vertical dipping method. UV light was irradiated on the LB films in vacuum for the polymerization of DA. The heat treatment was performed in air at 90 °C for 15 min in order to convert the polymerized blue DA to red one.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the pressure( $\pi$ )-area( A ) isotherms (at 20 °C) of mixed monolayers containing PHT and DA in various ratios. It should be noted that the abscissa (A) is based only on the number of DA molecules spread on the subphase. This figure therefore indicates the effect of the addition of PHT

on the  $\pi - A$  isotherm of DA. A is not so expanded by the addition of PHT while all of the mixtures of DA and PHT form stable monolayers on the subphase as shown from the steep rise in  $\pi$  with decreasing A. These results suggest that PHT molecules stack on themselves with increasing ratio of PHT to DA.

Clear X-ray diffraction patterns were obtained for all the LB films (29 layers) containing DA and PHT. The sharp reflection patterns can be observed before and after the UV irradiation and after the following heat treatment. These results indicate that the LB films have the regions of well defined layered structure. The bilayer distance of the LB films fabricated from the mixed monolayers is almost the same to that of the LB film consisting of only DA. It is considered that the regions of well defined layered structure are composed of DA. The other regions probably contain the PHT molecules stacked on themselves.

The molecular orientations of DA and PHT were also investigated by FT-IR (Reflection Absorption Spectroscopy and Transmission technique) and SHG (Maker fringe method) measurements. We will discuss the structure of the LB films by combining these results.

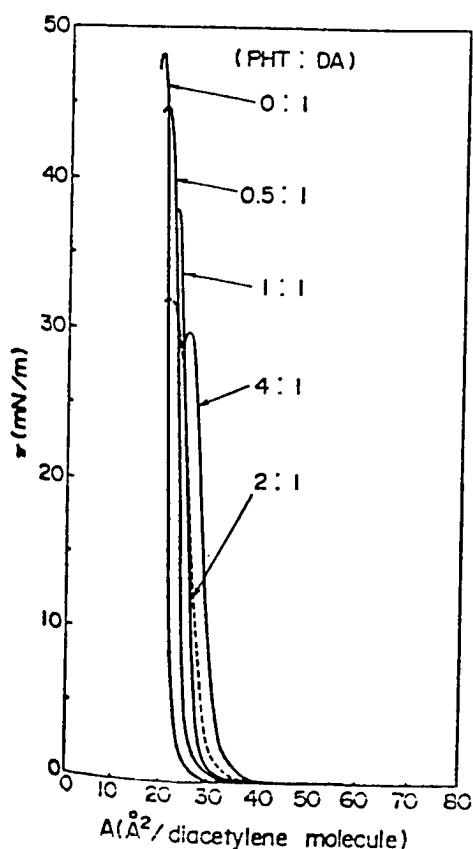


Fig.1 Surface pressure( $\pi$ )-area per diacetylene molecule(A) Isotherms for the mixtures of poly(3-hexylthiophene)(PHT) and pentacosa-10, 12-diynoic acid (DA).

STRUCTURAL AND PHOTOCHEMICAL PROPERTIES OF MONOLAYER  
ASSEMBLIES CONTAINING HETEROAROMATICS

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We have been making efforts to achieve vectorial electron transfer reactions by the use of organized monolayer assemblies composed of a photoreaction center model and redox compounds. The structural characterization such as molecular orientation, distance, and electronic interactions both at the ground and the excited states of functional groups is essential for such studies. We reported the molecular orientation and interactions at the ground state of carbazolyl chromophores in mixed monolayer assemblies containing 11-(9-carbazolyl)undecanoic acid (CUA).<sup>[1]</sup> We now report the aggregation and photochemical properties of monolayer assemblies containing heteroaromatic chromophores.

A pure CUA sample synthesized by us and a commercial CUA sample (denoted as MP-CUA) containing a very small amount (470 ppm) of 5H-benzo[b]carbazolyl derivatives (BCZ) were used. 1,3-Dihexadecylalloxazine (DHA) which has a chromophore as a hydrophilic group was also prepared. Palmitic or arachidic acids (abbreviated to PA or AA, respectively) were used after repeated recrystallization from ethanol. Mixed monolayers of MP-CUA with PA (1:19, 1:9, and 1:2.7) or AA (1:4) were deposited at 20 mN·m<sup>-1</sup> and 15 °C or 20 °C, respectively. Mixtures of CUA and PA (CUA fraction : 2-40%) were deposited at 15°C and 20 mN·m<sup>-1</sup>. A mixture of DHA and AA (1:5) was deposited at 18 °C and 20 mN·m<sup>-1</sup>.

In addition to the fluorescence of carbazolyl chromophores at 360 and 372 nm, fluorescence peaks at 417 and 442 due to BCZ were observed in mixed monolayer assemblies containing MP-CUA more than about 5%. The intensity ratio of the emission of BCZ ( $I_A$ ) and the emission of carbazolyl

groups ( $I_D$ ) increased steeply with the fraction of MP-CUA above about 5% and tended to saturate at higher fraction ( $\sim 27\%$ ). No fluorescence due to BCZ by direct excitation at 390 nm was observed in mixed monolayers. These results indicated the very efficient energy transfer from carbazolyl chromophores to BCZ in monolayer assemblies. From the red-shift of the absorption spectrum of mixed monolayer assemblies of MP-CUA, it was shown that carbazolyl chromophores were aggregated to such an extent as making interactions of their transition dipole moments possible.[1] The fluorescence of CUA in mixed monolayer assemblies gradually red-shifted with a CUA fraction upto about 20%. The efficient energy in mixed monolayer assemblies of MP-CUA was analyzed by the singlet exciton transfer model.[2] The number of jumps during the lifetime without acceptors was evaluated to be 1600, 1400, 700, and 45 for 1:2.7, 1:4, 1:9, and 1:19 mixtures, respectively.

The fluorescence of CUA in mixed monolayer assemblies decreased upon excitation both in air or in Ar environments by a Xe-lamp (mainly at 290 nm, 1 mW/cm<sup>2</sup>). The fluorescence intensity showed a rapid decrease at the initial stage ( $\sim 10$  min) followed by a very gradual decrease in air. The extent of fluorescence decay increased with increasing the mole fraction of CUA or the intensity of light. No effects of excitation wavelength were found. The fluorescence did decrease in Ar, too, somewhat slowly, which strongly suggested that the photooxidation of carbazolyl groups was not the only process responsible for a CUA system. Mixed monolayer assemblies of DHA containing electron-accepting alloxazine chromophores also showed similar fluorescence decay upon irradiation at 380 nm. From these results, the fluorescence decay observed in mixed monolayer assemblies was most probably caused by photoinduced structural changes of aggregates and by the efficient energy transfer to non-fluorescent sites formed in such processes. Similar fluorescence decay was reported in vacuum-deposited pyrene derivatives.[3]

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STRUCTURAL CONTROL AND CHARACTERIZATION IN MIXED AND ALTERNATE  
LB FILMS OF SIMPLE LONG-CHAIN COMPOUNDS

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Simple amphiphilic compounds such as long-chain fatty acids and esters are very useful as matrix materials in fabricating functional monolayer assemblies. Previously, we reported conditions for formation and structural characterization of these simple LB films.<sup>1, 2)</sup> Both X- and Y-type depositions can be achieved with the salts and esters of long-chain fatty acids depending on physical conditions such as temperature, surface pressure and pH of subphase, as well as chemical structures of the film materials. However, from the X-ray long spacings, the LB films of salts and methyl esters take only the head to head structure, while ethyl esters have the head to tail structure as the final stable form, irrespective of the deposition types.

In this work, we have examined the control and characterization of molecular arrangements in the mixed and alternate LB films of the above-mentioned compounds by X-ray diffraction using a Weissenberg camera.

The alternate monolayer assembly of methyl arachidate and palmitate showed a long spacing of 48.1 Å, which is just the mean value of 52.9 Å for arachidate and 43.3 Å for palmitate films. On the other hand, in the assemblies of mixed monolayers of methyl arachidate and palmitate, since a difference in the molecular length between two esters is large as 5.1 Å, some free spaces seems to be remained in the films. The X-ray diffraction patterns of the mixed films in various molar ratios indicated that these films take a two-phase structure. One is crystallite with polar group planes parallel to the film plane, and the other is inclined at a definite angle.

The assembly of mixed monolayers of polymerizable vinyl stearate and unreactive methyl ester is worth remarking. Vinyl stearate take only the head to tail structure with long spacing of 25.2 Å in the LB films. However, in the equimolar mixed film with methyl stearate (long spacing of 47.9 Å) the head to head structure with long spacing of 49.4 Å can be achieved as the stable state.

For the assembly of mixed monolayers of Pb(II) stearate and ethyl stearate, it has been found that the spacing between Pb planes can be controlled by mixing ratios with ethyl ester, and the transition from the head-to-head to the head-to-tail structure occurs at about 80 molar percent of ethyl stearate (Fig.1).

Thus, the structure of functional LB films can be controlled by the selection of matrix molecules and the composition.

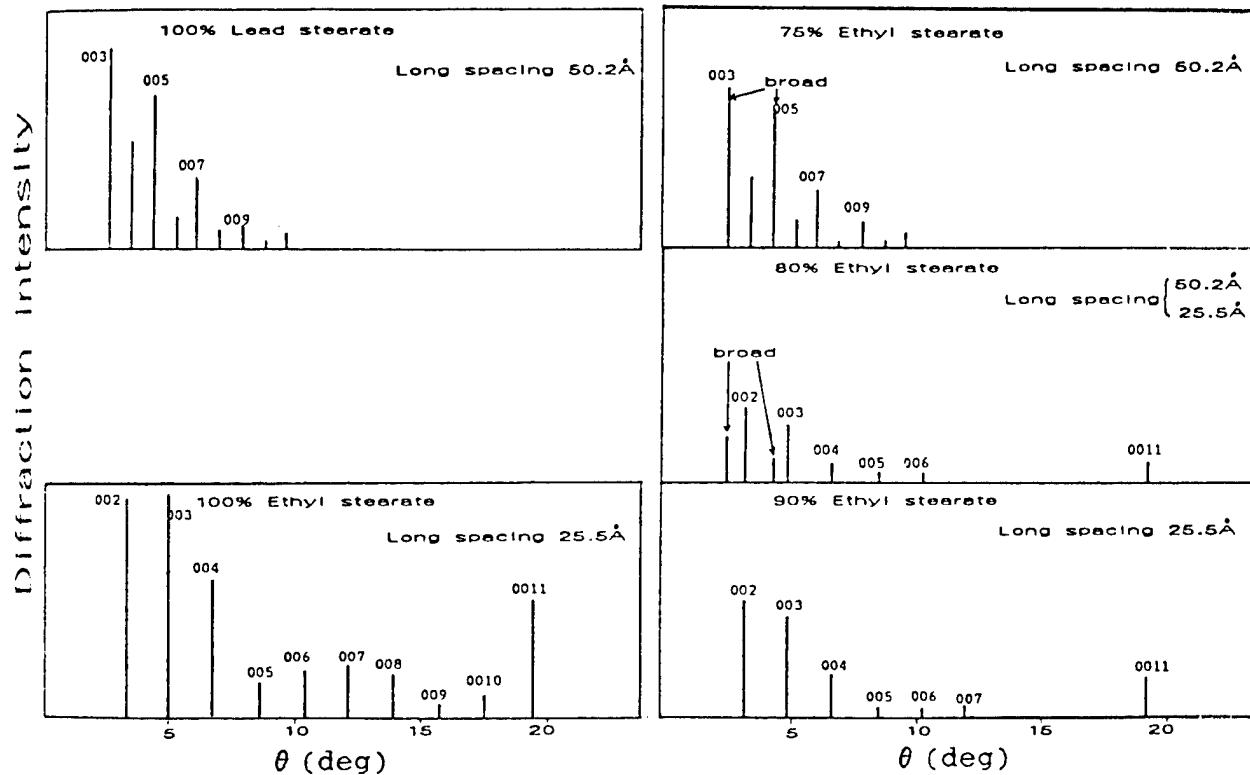


Fig.1. X-ray diffraction patterns of mixed LB films of lead and ethyl stearate. Diffraction intensity was evaluated from a densitometry measurement of each spot on the equatorial Weissenberg photographs.

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# Molecular Orientation in Alternating LB Films Studied by FT-IR Transmission and Reflection-Absorption Spectroscopy

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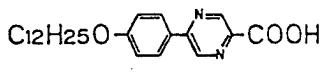
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In recent years, much attention has been paid to Langmuir-Blodgett (LB) films with alternate layers of two different materials. They have noncentro-symmetric structures and are expected to give piezoelectric, pyroelectric, and non-linear optical effects. These effects are entirely depend on the molecular structure of the films. Recently, we have proposed a quantitative evaluation method of molecular orientation in thin LB films through the comparison of infrared transmission and reflection-absorption (RA) intensities<sup>1)</sup>. In the present work, we applied this method to the study of molecular orientation in alternating LB films of 5-(p-dodecyloxyphenyl)pyrazine-2-carboxylic acid (DOPC) possessing a large dipole moment along the molecular axis and fully deuterated stearic acid C<sub>17</sub>D<sub>35</sub>COOII (St-d<sub>35</sub>).

The spread monolayers of DOPC and St-d<sub>35</sub> on water were transferred alternately on ZnSe plates (for transmission measurements) or on glass slides which had been vacuum-evaporated with a 100nm-thick silver film (for RA measurements) at the surface pressure of 30 mN/m. St-d<sub>35</sub> was transferred on the up stroke, DOPC on the down stroke. In the case of barium salt LB films, water containing 2x10<sup>-4</sup>M BaCl<sub>2</sub> was used as a subphase. All infrared measurements were recorded on a Nicolet Model 6000C FT-IR spectrophotometer and coadded 3000 scans with the resolution of 4 cm<sup>-1</sup>. For RA measurements, the *p*-polarized radiation was incident on the sample at 85° off the surface normal.

Figures 1 and 2 represent the infrared transmission and RA spectra of the alternating films of barium salts, respectively. S(PS)n means that the alternating layers of DOPC(P) and St-d<sub>35</sub>(S) were deposited n times on the first monolayer of S. The antisymmetric and the symmetric CH<sub>2</sub> stretching bands of DOPC (2920, 2852cm<sup>-1</sup>), the antisymmetric and the symmetric CD<sub>2</sub> stretching bands of St-d<sub>35</sub> (2193, 2088cm<sup>-1</sup>), and the antisymmetric COO<sup>-</sup> stretching bands of DOPC and St-d<sub>35</sub> (1608, 1514cm<sup>-1</sup>) had much stronger intensities in the transmission spectra than in the RA spectra, while the opposite was seen for the symmetric COO<sup>-</sup> stretching bands of St-d<sub>35</sub> and DOPC (1430, 1409cm<sup>-1</sup>). This



fact reveals that the molecular axis and the bisector of the carboxylate group of respective molecules orient almost normal to the film plane.

Using the previously proposed method<sup>1)</sup>, we evaluated the tilt angles of the hydrocarbon-chain axes  $\gamma$  and the bisectors of the carboxylate groups  $\phi$  of DOPC and St-d<sub>35</sub> molecules to the surface normal in the S(PS)<sub>n</sub> barium salt film as follows :  $\gamma_{DOPC} = 38^\circ$ ,  $\phi_{DOPC} = 28^\circ$ ,  $\gamma_{St-d_{35}} = 20^\circ$ ,  $\phi_{St-d_{35}} = 23^\circ$ . These angles were almost the same as the corresponding values obtained for the homogeneous LB films of each salt. This suggests that the molecular orientation in this alternating LB film of barium salts is mainly governed by the intermolecular interaction among neighboring molecules in the same layer.

Similarly, we calculated the tilt angles of the hydrocarbon-chain axis of both molecules in the S(PS)<sub>n</sub> acid film as follows :  $\gamma_{DOPC} = 49^\circ$ ,  $\gamma_{St-d_{35}} = 35^\circ$ . These angles were larger than the corresponding values obtained for the same alternating LB films of barium salts and those obtained for the homogeneous LB films of each acid. These facts reveal that in the alternating films of acids, intermolecular interaction among neighboring molecules in the same layer is weaker as compared with that in the corresponding alternating films of barium salts, and that interaction between DOPC and St-d<sub>35</sub> in the adjacent layers is weaker than that between the same molecules in the adjacent layers.

Now, measurements of the pyroelectric effects of these alternating films are progressing. Correlation between structure and pyroelectricity will be discussed elsewhere.

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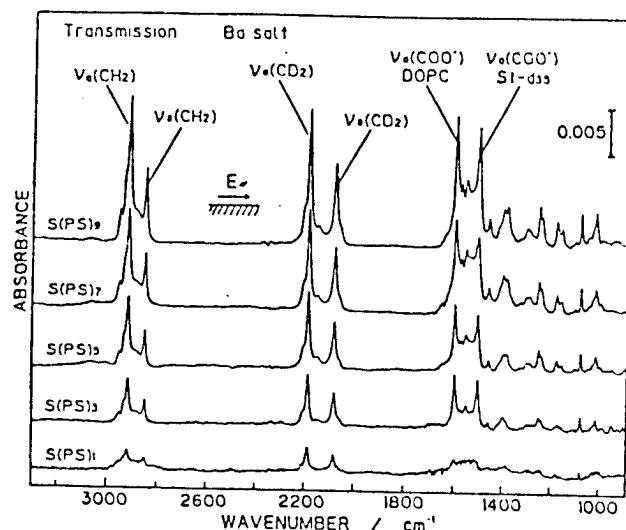


Figure 1. Infrared transmission spectra of the S(PS)<sub>n</sub> barium salt LB films consisted of the alternate layers of DOPC(P) and St-d<sub>35</sub>(S) deposited n times on the first S monolayer.

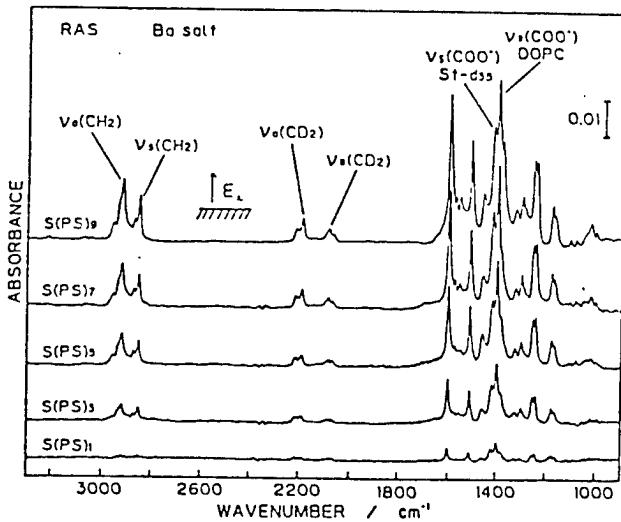


Figure 2. Infrared RA spectra of the S(PS)<sub>n</sub> barium salt LB films.

STRUCTURE OF LB 'SUPERLATTICES' WITH VARIOUS  
SEQUENCES OF ALTERNATING LAYERS

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The LB technique allows the alternate deposition of monolayers of various amphiphilic molecules to be carried out [1]. These layered assemblies are promising for the creation of some elements of molecular electronics. It is important to develop methods for the identification of similar 'superlattices' and to study peculiarities of their structure.

In this work, LB films containing bilayers of two types of molecules alternating in various sequences were studied by low-angle X-ray diffraction. In the case of assemblies containing barium behenate (B) and VO tetra-3-octadecylsulphamoylphthalocyanine (V) bilayers the sequences of alternation were the following: BVBVBV... (1), BVVBVVBVV... (2), BVVVBVVV... (3), BVVVVBVVV... (4), BVVVVVBVVVVV... (5), BBVBBVBBV... (6), BBBVBBV... (7). The films of barium behenate (B) and Cu tetra-3-octadecylsulphamoylphthalocyanine (C) were deposited only in the sequence BCBCBC... (8). Three types of barium behenate (B) and octadecen-1-ylphenol (P) assemblies BPBPBP... (9), BPPBPPBPP... (10), BPPPBP... (11) were also investigated. Some results are given in the Table 1. Clear alternation of bilayers in a given order takes place for all samples, no bulk crystallites are found. Crystalline order along the normal to the layer plane is preserved at distances of 70-120 nm.

The influence of X-ray refraction, finite size of the Ewald sphere and crystalline structure peculiarities on the shift of Bragg maxima was taken into account to obtain the exact values of periods. We have found that the shift caused by X-ray refraction is considerable, if the Bragg angles are less than 1 degree. Suddenly, we have noticed that the additive character of the summation of monolayer thicknesses in deposited films 1 - 7 doesn't take place. The periods of all the 'superlattices' investigated are smaller than the sums of the respective number of periods of monocomponent LB films. The observed deviation from additivity is greater the greater the number of bilayers within one period. The values of deviations in the case of 'superlattices' 2 and 6 (as well as 3 and 7) are approximately equal to each other. The periods of the 'superlattices' 9 - 11 turned also to be less than the correspon-

Table 1. Parameters of structure of LB films.

Film type	Composition of period	Period (nm) Experimental	Period (nm) Calculated	Number of reflections
-	B	5.80+0.05	-	14
-	V	4.1+0.1	-	1
-	C	4.1+0.1	-	1
-	P	4.77+0.05	-	10
1	BV	9.74+0.08	9.9	12
2	BVV	13.60+0.14	14.0	10
6	BBV	15.20+0.18	15.7	19
3	BVVV	17.1+0.2	18.1	9
7	BBBV	20.8+0.3	21.5	17
4	BVVVV	20.1+0.4	22.2	11
5	BVVVVV	25.2+0.4	26.3	13
8	BC	9.74+0.08	9.9	12
9	BP	10.4+0.2	10.57	7
10	BPP	15.0+0.3	15.34	13
11	BPPP	19.94+0.30	20.13	12

ding sums of the monocomponent film periods. But the difference is small and is approximately equal to the error of measurement. So, the deviation from additivity in the case of LB films 1 - 7 can be caused by the use of amorphous phthalocyanine layers and by the rearrangement of barium behenate crystalline structure.

To clarify this situation the distributions of electron density along the axis normal to the layer plane were determined for all mentioned above 'superlattices'. Calculation of Fourier transforms was made under condition of constant electron density in the region of hydrocarbon chaines of barium behenate bilayers. High-frequency filtration was used to decrease the distortion of calculated functions [2]. The analysis of the determined electron density distributions leads to a conclusion that the revealed deviation from additivity is due to diminishing of thicknesses of all hydrophobic regions within the period. This can be caused by the increase of tilt of the hydrocarbon chaines.

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# ACID VAPOR TREATMENT OF FATTY ACID SALT LB FILMS

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Secondary treatments of LB films have been proved to be the powerful tools in modifying their properties. In LB films of merocyanine dye derivative mixed with cadmium arachidate, the dissociation and the restoration of the J-aggregates have been found to be controlled by the treatments with heat (HT), acid and base (AT and BT, respectively),<sup>1)</sup> which simultaneously cause drastic change in X-ray diffraction patterns.<sup>2)</sup> These changes in X-ray patterns are also recognized in LB films of Cd- or Ba- salt of fatty acids. We report here the results of a study of acid vapor treatment (AT) on fatty acid salt LB films.

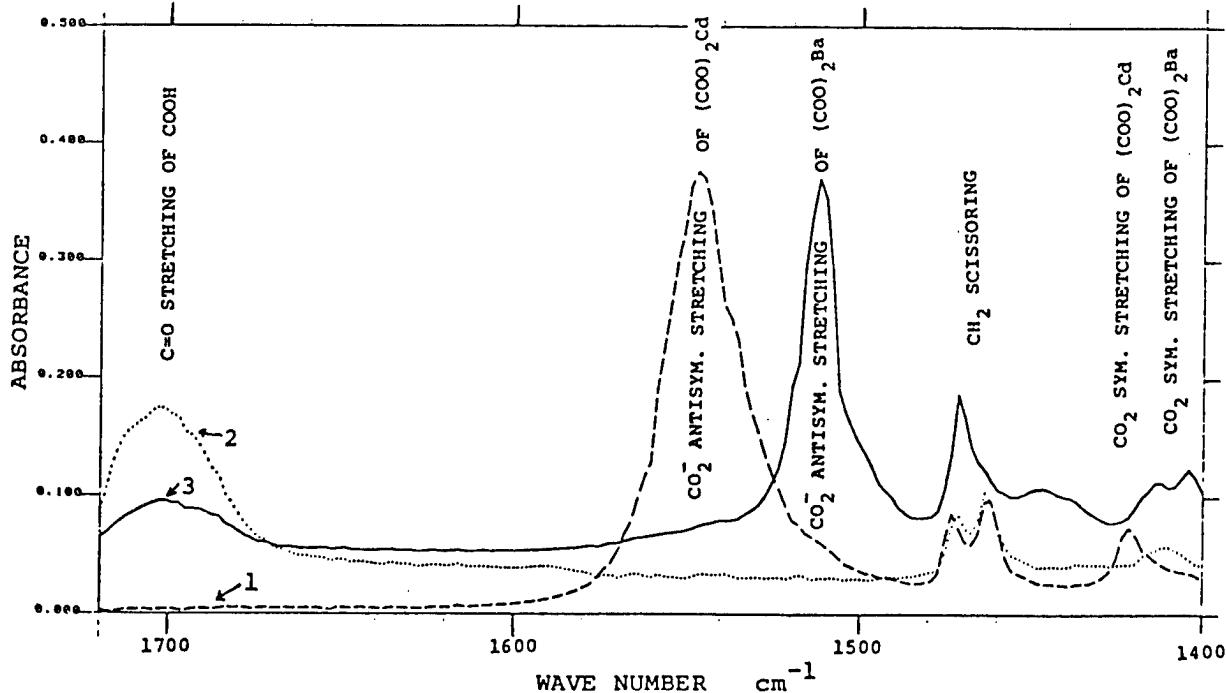
When LB films of M salt ( $C_n(M)$ , where M is a divalent metal ion) of normal fatty acid,  $CH_3(CH_2)_{n-2}COOH$  ( $C_n(H)$ ), are exposed to the atmosphere vaporized from volatile acid at room temperature, every (00l) Bragg peak based on LB lamellar structure decreases in height with the exposure time without any appreciable change in both the peak width and the diffraction angle, and it finally disappears except for a couple of small-angle peaks and increased broad background. On the contrary no notable change is observed for AT in the corresponding  $C_n(H)$  LB films.

Figure 1 shows the ir absorption<sup>3-6)</sup> for a  $C_{20}(Cd)$  LB film formed on  $CaF_2$  substrate ( $CaF_2/C_{20}(Cd)$ ) before and after AT (HCl vapor). In the as-deposited case the  $CO_2^-$  antisym. stretching peak of  $(COO)_2Cd$  is seen (curve 1). After AT this peak disappears and the C=O stretching peak of COOH appears, while the peaks related to the vibrations of  $CH_2$  and of  $CH_3$  do not change appreciably (curve 2). These experiments give evidence that the LB lamellar structure is not destroyed by AT, but only the divalent metal ions have been liberated from the carboxylates.

In addition to the decrease in X-ray (00l) peaks, new characteristic diffraction peaks appear depending on the metal ion species of the carboxylates.<sup>2)</sup> We have not found any materials which have similar structures as these new peaks. And

we have not observed any ir absorption peaks which are responsible for these new X-ray diffraction peaks. Although the origin of these new peaks is not clear for the moment, the species of metal ions that have been constituents of the carboxylates of the  $C_n(Cd)$  before AT, can be identified using this effect. Superposition of the X-ray diffraction patterns characteristic of  $C_{20}(Cd)$  and of  $C_{20}(Ba)$  is observed, when an LB film ( $CaF_2/C_{20}(Cd)$ ), in which metal ions have been released from the carboxylates by AT in advance) is soaked in a solution containing  $Ba^{2+}$  ions. This experiment suggests that the protons of the carboxyls of the film have been substituted by the  $Ba^{2+}$  ions. The substitution is also confirmed by ir absorption. The  $C=O$  stretching peak decreases and the  $CO_2^-$  antisym. stretching peak appears by soaking the film that has been subjected to AT (curve 3).

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# INFLUENCE OF SUBSTRATE SURFACE ON L-B MULTILAYERS

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Building-up of structurally high quality L-B films is essential to study properties of the films and to get reproducible data. The high quality L-B films are obtained under optimum experimental conditions. One of them will be a physical and chemical state of a substrate surface. We have examined the stacking structure of cadmium stearate L-B films under control of wettability and coarseness of the substrate surface by chemical and physical treatment.

The glass slide substrates were treated with a series of the following ways. (i) Immersing the substrate in  $H_2SO_4$  for 24 hr (● in fig. 1), followed by hydrophobic treatment with hexamethyldisilazane (○). (ii) Treating with  $H_2SO_4/H_2O_2$  or abrasive of 0.05, 0.3 or 3  $\mu m$  mean diameter (x). After the above treatments, the glass plates were rinsed in an ultrasonic cleaner with pure water, ethanol, and chloroform successively. The wettability of the substrate was evaluated by the contact angle of pure water, and the coarseness of it was done by the mean diameter of the abrasive for convenience. The x-ray diffraction line width of the lamellar repeat were measured to evaluate the stacking order from diffraction line width.

Figure 1 shows the relationship between the contact angle and the line width (in FWHM) of the 2nd order diffraction. It is seen that in the intermediate surface wettability the stacking order tends to be worse than that for more hydrophilic or hydrophobic surface state (substrate treated by method (i)). The figure also shows that the rather corrosive surface treatment (method (ii)) hinders the regular piling up of the monolayers, which is represented by the broadening of the diffraction line compared to that obtained by the surface treatment of (i) even when the contact angle is similar. Fig. 2 shows the

influence of wettability and coarseness of substrate surface on the stacking order of L-B films more evidently. Though this result leads to a somewhat natural conclusion that the surface of a substrate should be smooth and hydrophilic hydrophobic, it is suggestive for the further investigation of the influence of surface state on the order of stacking.

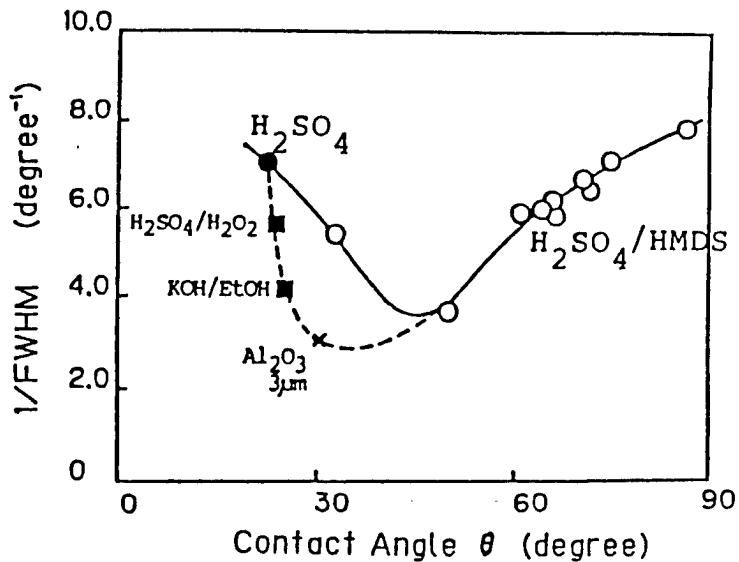


Fig.1 Dependence of the diffraction line width upon the wettability of the substrate surface. 41 layers of cadmium stearate monolayers were deposited on each substrate.

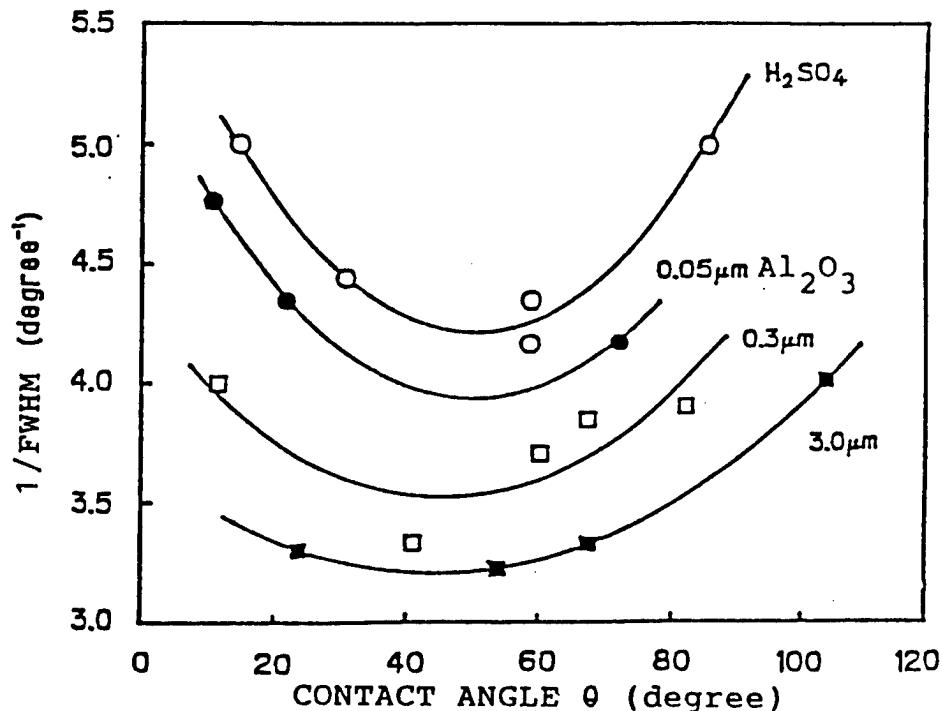


Fig.2 Influence of the wettability of substrate surface on stacking order for several substrate roughness. The number of layers was 20 or 21.

# Evaluation for the Stability of LB Films at the air-water interface or in Water by using a Piezoelectric Crystals

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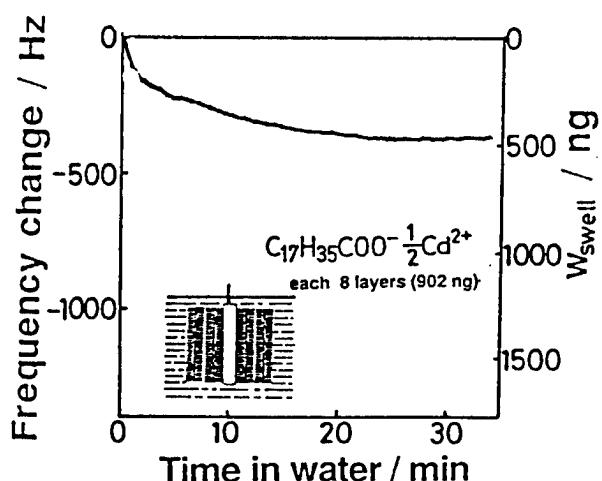
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Characterizations of Langmuir-Blodgett (LB) films have been widely studied in the dry state by various methods such as FTIR spectra, X-ray diffraction, and XPS analysis. However, the evaluation for the stability of LB films in water or at the air-water interface has not been fully explored. We have found by means of a piezoelectric substrate that LB films of cadmium stearate were deposited on the substrate with much water which gradually evaporated through the layers of the films when exposed to air.<sup>1)</sup>

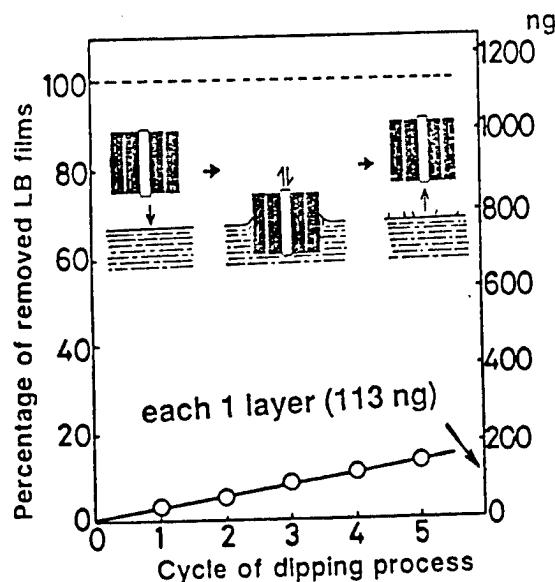
In this paper, we study a swelling behavior in an aqueous phase and a removal behavior at the air-water interface of LB films by using a piezoelectric crystal plate as a substrate. A piezoelectric crystal is known to provide very sensitive mass measuring devices in ng-levels because the resonance frequency decreases upon the deposition of a given mass on the crystal electrode. LB films of cadmium stearate were transferred on a piezoelectric crystal (9 MHz, AT cut quartz on which Ag electrodes had been deposited on both sides).

When the LB film on the crystal immersed in the distilled water, the frequency decreased largely with time and leached an equilibrium value after 10-60 min. This means that the apparent weight of LB films increases due to the swelling by the penetration

of water into the interlayers. When the LB film on the crystal was lowered and raised through the air-water interface, the frequency decreased with each cycle, which indicates the removal of LB films from the crystal at the air-water interface. The amount of the removed LB films decreased with the increase of the alkyl chain length of aliphatic acid from  $C_{16}$  to  $C_{22}$ . In the case of the polymerized LB films, the removal at the air-water interface was hardly observed. The swelling behavior in an aqueous phase and the removal behavior at the air-water interface were examined under different conditions such as temperature of a subphase, dipping speed, surface pressure, and number of layers.



Swelling of LB films in water (20 °C)



Effect of dipping cycle on removal of LB films (20 °C)

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# Detection of Phase Transition of LB films by a Piezoelectric Crystal

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When lipid LB films are used as a model of biological membranes, it is important to evaluate the physicochemical properties of LB films in water.

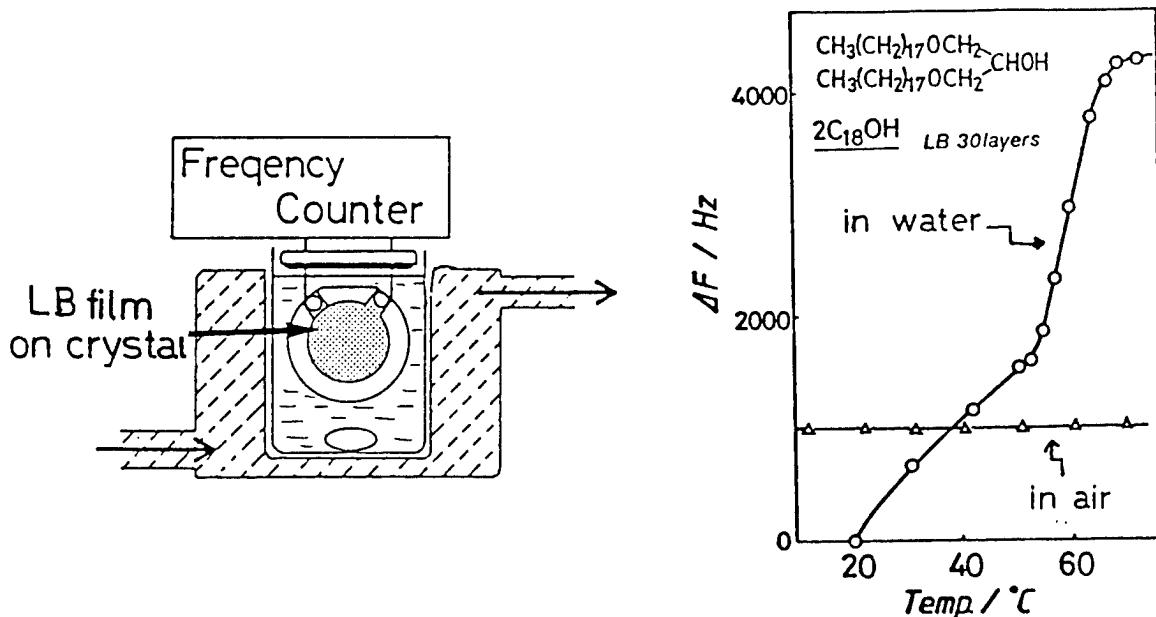
In this paper, we report the detection of phase transition behavior of LB films in water by using a piezoelectric crystal as a substrate. Although piezoelectric crystals are known to provide very sensitive mass measuring devices because of resonance frequency changes upon the deposition of a given mass on the crystal electrode, we find that the frequency of the crystal is also sensitive to the elasticity change of the LB films on the electrode in aqueous phases.

LB films of dialkyl-type amphiphiles,  $2C_{18}OH$ , were transferred as a Y type 30 layers on a piezoelectric crystal (9 MHz, AT cut, 8 x 8 mm) and immersed in water. As shown in Figure 1, when the temperature of water phase increased with time, the frequency of the LB film-deposited crystal largely increased (the mass decrease) near 55-60 °C, the frequency reverted to the original value when the temperature decreased near room temperature. It was confirmed from the frequency measurement in air before and after temperature changes in water that LB films did not peeled off from the crystal substrate.

- i) Crystal powder of  $2C_{18}OH$  showed a sharp endothermic peak near 55-60 °C in water by differential scanning calorimetry (DSC) in water, which indicates the phase transition temperature ( $T_c$ ) from solid to liquid crystal state.
- ii) The frequency increase of  $2C_{18}OH$  LB films near 55 °C was not observed in air.
- iii) LB films swelled largely near 55 °C compared with 20 and 70 °C in water.

From these findings, the frequency enhancement near 55 °C can be explained as follows. The solid LB films vibrate with the crystal plate at temperatures below  $T_c$  and the frequency respecting to the mass on the electrode is observed. At and above the phase transition temperature, the LB membranes become fluid and water penetrates into interlayers near hydrophilic head groups (swelling). The outer layers of fluid and swelled LB films cannot oscillate with the crystal plate due to slipping between layers. As a result the frequency increases at  $T_c$ , because the only inner part of LB films vibrate with the crystal plate and the elasticity of the membrane changes.

In conclusion, the piezoelectric crystal will become a new tool to detect the membrane fluidity on the crystal, in addition to the detection of the mass change by the adsorption of substances from outside.<sup>1)</sup>



Frequency changes of LB films-deposited piezoelectric crystal depending on phase transition

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Direct Observation of the Surface Structure of LB Films by Scanning  
Electron Microscopy

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The existence of short-circuit paths in LB films was indicated by an investigation on electrical transport properties of MIM and MIS devices incorporating the films.<sup>1</sup> Further diagnosis of the film structure, therefore, has been in need of a direct microscopic analysis. Although a number of TEM studies on LB films have been made<sup>2</sup>, the peculiarity in sample preparation kept away the direct observation of a film formed on a practical device substrate. On the other hand, very few studies on SEM have been made in spite of the advantage that it tolerates any sample structure. The reason has been that a high-resolution image of an insulating material could hardly be obtained by a conventional "high-voltage" SEM, and that a thin metal coating which will surely deteriorate the surface structure was unavoidable to prevent the charge-up effect. In order to obtain both a direct and a clear image of the LB film, it was required to extend the observation condition to a lower accelerating voltage and to find the optimum condition. In this study, the variation in the secondary electron image of the film according to the observation condition was investigated by making use of a new apparatus<sup>3</sup>, equipped with electron-optics operating at a low accelerating voltage and a field emission gun to reduce chromatic aberration. As a result, we succeeded in the direct observation of LB films without metal coating, for the first time.

The samples were non-coated fatty acid films prepared by the vertical deposition method on oxidized Si wafers( $\text{SiO}_2$ , 2000Å). SEM micrographs were obtained at a tilting angle of 40° with magnifications ranging from 50,000 to 100,000. As a result, only large structures (several hundred Å) were observed at high voltage, but fine film structures with uneven surface came out in the image as the voltage decreased. Finally, 1.5 kV accelerating voltage( $V_0$ ) and 3pA probe current( $i_p$ ) was found to be the optimum condition for these

samples. Such a variation in the image according to the accelerating voltage is attributable to decreases in both the signal from the substrate and the charging of the film.

Figure 1 shows SEM micrographs of aluminum stearate multilayers (200 Å) deposited at different conditions so as to vary the dynamic surface pressure at the substrate during deposition.<sup>4</sup> A comparison of these micrographs indicates that a reduction in the difference ( $\Delta\pi$ ) between the static and dynamic surface pressures caused less deterioration of the film structure, which agreed with the results by x-ray diffraction analysis on the same films.

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2. N.Uyeda, et al., Nature, 327(1987)319.
3. HITACHI low accelerating voltage SEM, S-900.
4. T.Nakayama, et al., This extended abstract.

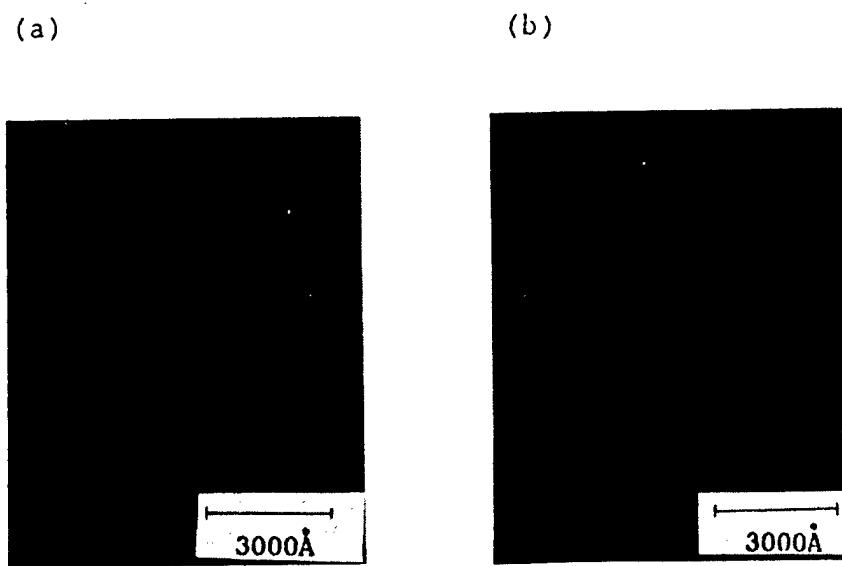


Fig.1 SEM micrographs ( $V_0 = 1.5$  kV) of aluminum stearate multilayers (200Å), deposited by two methods giving different  $\Delta\pi$  ( $\pi_{sub,s} = 21$  dyn/cm<sup>2</sup>); using usual trough (18x30 cm<sup>2</sup>), at dipping speed of 5 mm/min.  $\Delta\pi = 21$  dyn/cm<sup>2</sup>(a); using modified trough equipped with two moving barriers (9x6 cm<sup>2</sup>), at dipping speed of 0.5 mm/min.  $\Delta\pi = 3$  dyn/cm<sup>2</sup>(b)

Electron Microscopic Observations on Crystalline and Amorphous  
Monolayers of Fatty Acids

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It has been generally considered that the phase transition of monolayer from an amorphous to a crystalline state occurs owing to the compressing the monolayer. However, it was recently proposed that the crystalline monolayer domains were formed on the water surface even at zero surface pressure and were aggregated with increasing the surface pressure<sup>1)</sup>. In this study, the aggregation structure of monolayers composed of fatty acids with different alkyl chain length at various surface pressures was investigated by a transmission electron microscope(TEM).

Figure 1 shows the  $\pi$ -A isotherm for the behenic acid( $C_{22}$ ) monolayer spread on the water surface at the subphase temperature( $T_{sp}$ ) of 293 K, and the bright field images and the electron diffraction(ED) patterns of the monolayers at the surface pressures of 0, 20 and 35  $mN \cdot m^{-1}$ . The temperature of 293 K was below the melting point( $T_m$ ) of behenic acid monolayer<sup>2)</sup>. The  $\pi$ -A isotherm indicates a gas-solid coexisting system without appearance of a plateau. At 0  $mN \cdot m^{-1}$ , the bright field image and ED pattern showed an island structure with high contrast and a hexagonal spot, respectively. These indicate that two-dimensional crystalline domains grow right after spreading a solution on the water surface. With increasing the surface pressure, the bright field images represented the aggregating process of the two-dimensional crystallites, whereas the ED

pattern showed the hexagonal spot at every surface pressure. This molecular aggregation type was designated the crystalline monolayer.

Figure 2 shows the  $\pi$ -A isotherm for the myristic acid ( $C_{14}$ ) monolayer spread on the water surface at  $T_{sp}$  of 293 K, and the bright field images and the ED patterns of the monolayers at 0, 10, 15 and 23  $mN \cdot m^{-1}$ .  $T_{sp}$  of 293 K was above  $T_m$  of myristic acid monolayer<sup>2)</sup>. A plateau region on the  $\pi$ -A isotherm was observed, which indicated a solid-liquid coexisting system. At 0  $mN \cdot m^{-1}$ , the bright field image and ED pattern showed an island structure with low contrast and an amorphous halo, respectively. These indicate that isolated domains in an amorphous state grow right after spreading a solution on the water surface. Even though the monolayer was compressed up to the collapse pressure, it was still in an amorphous state without any phase transition from amorphous to crystalline state. This molecular aggregation type was designated the amorphous monolayer.

These results indicate that the aggregation structure of a fatty acid monolayer is mainly determined by the magnitude of  $T_{sp}$  and  $T_m$  of the monolayer.

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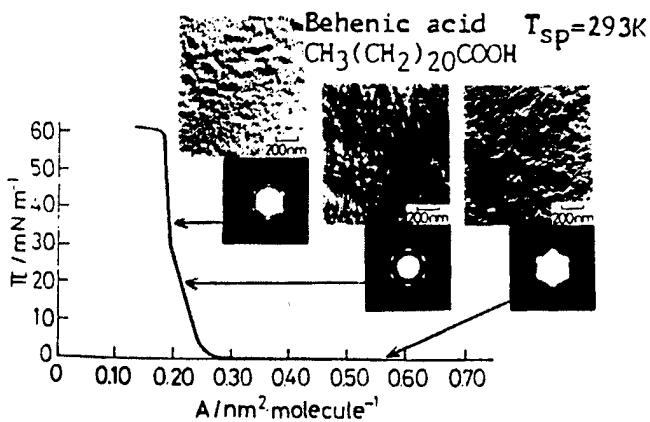


Fig. 1 Electron micrographs and ED patterns of behenic acid monolayer at 293 K.

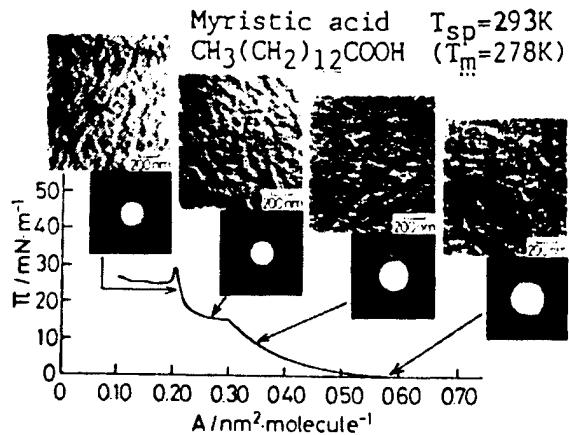


Fig. 2 Electron micrographs and ED patterns of myristic acid monolayer at 293 K.

## Morphology in Langmuir-Blodgett Multilayers of Nitroaniline Derivative - Fatty Acid Mixtures

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Langmuir-Blodgett multilayers containing oriented polar molecules with supporting or promoting molecules such as fatty acids were studied. Long-chain derivatives of *p*-nitroaniline (pNA) are attractive for polar molecules due to the large molecular polarizability of pNA. However, it is difficult to disperse these molecules uniformly in deposited films ascribing to aggregation of molecules [1]. We synthesized long chain derivatives of pNA such as *N*-stearyl-*p*-nitroaniline (st-pNA), *N*-stearoyl-*p*-nitroaniline (sto-pNA), and *N*-oleyl-*p*-nitroaniline (ol-pNA). Sto-pNA has a more hydrophilic group than st-pNA, and ol-pNA has an unsaturated bond in the alkyl-chain. Therefore, they are expected to be less aggregative than st-pNA. The surface morphology [2] of these mixed multilayers was evaluated by scanning electron microscopy (SEM). A mixed multilayer refers to the multilayer deposited using a mixture with arachidic acid ( $C_{20}$ ). As a result, we revealed that in sto-pNA mixed multilayers, aggregation is greatly reduced as compared with typical st-pNA mixed multilayers. Ol-pNA mixed multilayers could not be formed because of the phase separation of ol-pNA and  $C_{20}$ .

Figure 1 shows pressure-area isotherms of st-pNA mixed monolayers (a) and sto-pNA mixed monolayers (b). Each isotherm of the mixing ratio 1 : 0 shows a plateau or relaxation of surface pressure indicating that the monolayer is unstable. However, mixtures with  $C_{20}$  form condensed monolayers. The isotherms of sto-pNA monolayers of the mixing ratios 1 : 4 and 1 : 1 are nearly equal, which means that the occupied area per molecule of sto-pNA is nearly equal to that of  $C_{20}$ . In addition, these isotherms show no inflection similar to  $C_{20}$ , it indicates that the rearrangement of the sto-pNA molecules does not occur during the compression. IR spectra of transmission and RAS suggest that the sto-pNA molecules in the deposited film are oriented around normal to the substrate surface.

Figure 2(a) shows a SEM image of a st-pNA mixed multilayer deposited at 10 mNm<sup>-1</sup>, where many three dimensional aggregates are observed. The size and the density of the aggregates increase with the number of deposition. In deposited films at 30 mNm<sup>-1</sup>, a collapse of the film is also observed. On the other hand, in a sto-pNA mixed multilayer, such aggregates are not observed as shown in Fig.2(b). Uniformly mixed multilayers are obtained by substituting amido group for amino group in st-pNA. It suggests that the balance of the hydrophilicity and the hydrophobicity of sto-pNA is suitable for uniform mixing with  $C_{20}$ .

Figure 3 shows the absorption spectra of mixed multilayers in comparison to each spectrum of the pNA derivatives in a non-polar solvent of *n*-hexane. In the st-pNA case (a), the spectrum around 345 nm of the solution shifts considerably to the longer wavelength in the multilayer. This implies formation of aggregates. On the other hand, in the sto-pNA case (b), the shift of the spectrum is less than 10 nm. Moreover, the sto-pNA mixed multilayer is transparent in the visible spectrum region.

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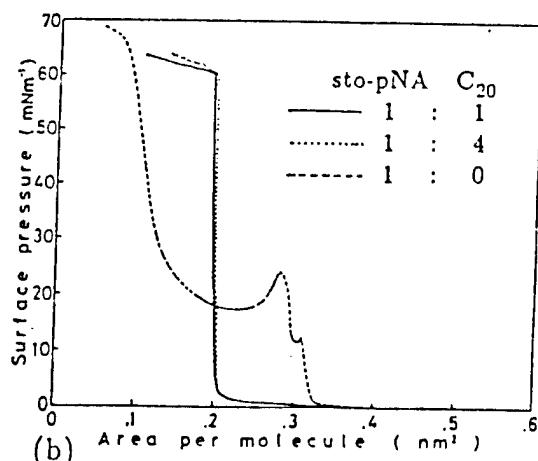
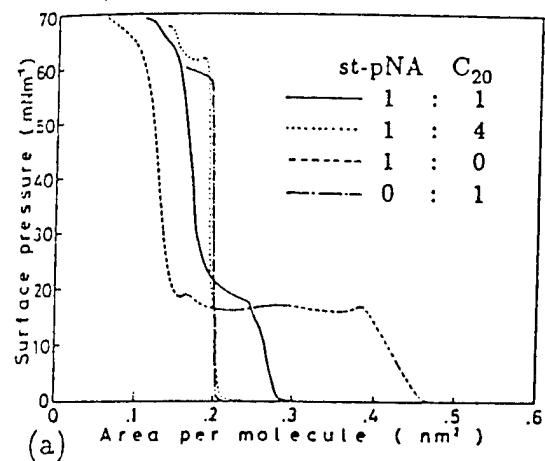
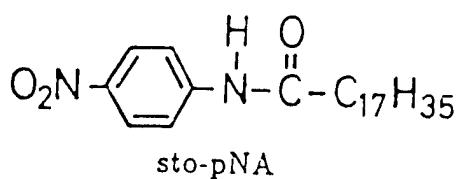
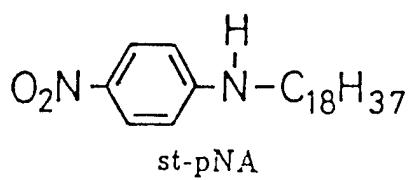


Fig.1. Pressure-area isotherms of nitroaniline derivative-fatty acid mixtures with different molar ratios on an aqueous subphase containing  $\text{Cd}^{2+}$  ions at  $19^\circ\text{C}$ , pH 6.8 in a compression speed of  $0.017 \text{ nm}^2 \text{ min}^{-1}$ : (a) mixtures of st-pNA and  $C_{20}$ ; (b) mixtures of sto-pNA and  $C_{20}$ .

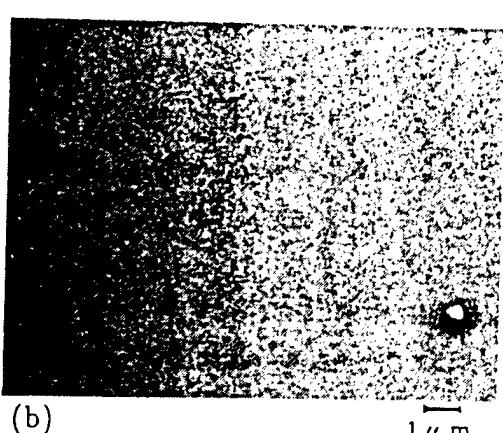
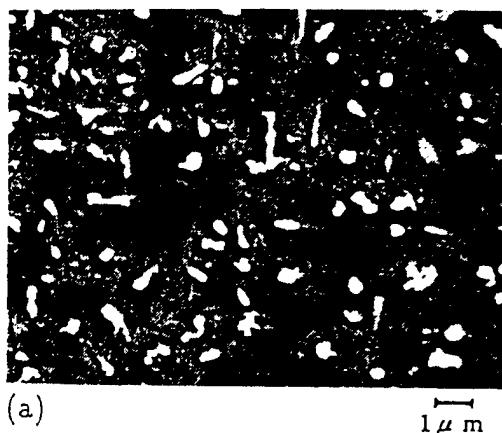


Fig.2. Scanning electron micrographs of LB multilayers deposited on glass substrates: (a) 29 layers of st-pNA :  $C_{20}$  = 1 : 1, at  $10 \text{ mNm}^{-1}$ ; (b) 31 layers of sto-pNA :  $C_{20}$  = 1 : 1, at  $30 \text{ mNm}^{-1}$ .

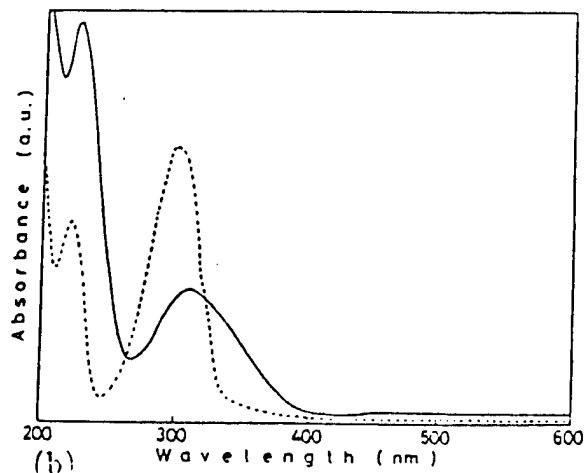
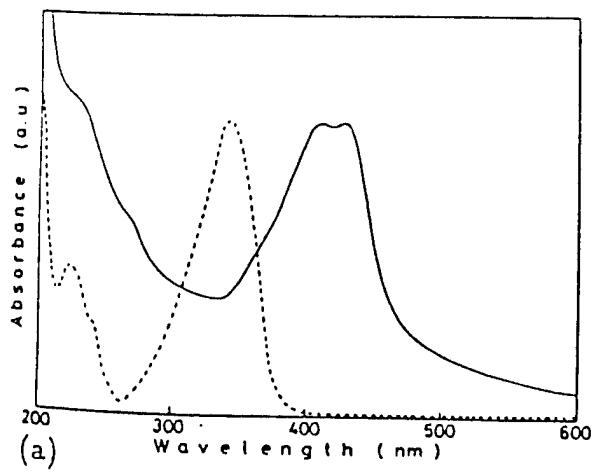


Fig.3. Absorption spectra of LB multilayers deposited on  $\text{CaF}_2$  substrates at  $19^\circ\text{C}$ , pH 6.8,  $30 \text{ mNm}^{-1}$  (—) and of n-hexane solution (---): (a) 13 layers of st-pNA :  $C_{20}$  = 1 : 1 and hexane solution; (b) 31 layers of sto-pNA :  $C_{20}$  = 1 : 1 and hexane solution.

# X-Ray Analyses on Structural Defects in Langmuir-Blodgett Film

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For an interesting application of Langmuir-Blodgett(LB) films to functional ultrathin organic films, it is indispensable to estimate the structural defects and crystalline dimensions in LB films and also, to investigate the procedure for constituting "defect-free" LB films. In this study, the crystallite size and distortion along the parallel(lateral) and normal(longitudinal) directions to the layer plane of LB films were quantitatively evaluated on the basis of x-ray measurements. The effects of the preparation conditions and of the chemical structure of LB films on these structural parameters were also discussed.

Crystallite size  $L_{lat}$  and crystalline distortion  $D_{lat}$  along the lateral direction in LB films were estimated by a modified single line method<sup>1)</sup> based on the Fourier analysis of wide angle x-ray diffraction profiles. Layer sequence  $L_{long}$  and interlayer distortion  $D_{long}$  along the longitudinal direction in LB films were calculated from the integrated width of the 001 small angle x-ray scattering peaks on the basis of the Hosemann paracrystal analysis<sup>2)</sup>.

Figure 1 shows the magnitude of  $D_{lat}$  and  $D_{long}$  for the barium palmitate( $2C_{16}Ba$ ), barium stearate( $2C_{18}Ba$ ), barium arachidate( $2C_{20}Ba$ ), and barium behenate( $2C_{22}Ba$ ) LB films prepared at the surface pressures where each monolayer is morphologically homogeneous<sup>3)</sup>, 20, 30, 30, and  $35 \text{ mN}\cdot\text{m}^{-1}$ , respectively. The magnitude of  $D_{lat}$  decreased with an increase of the alkyl chain length. This indicates that an increase of intermolecular force corresponding to an increase of the alkyl chain length enhances the regularity of crystalline phase in LB films. The magnitude of  $D_{long}$

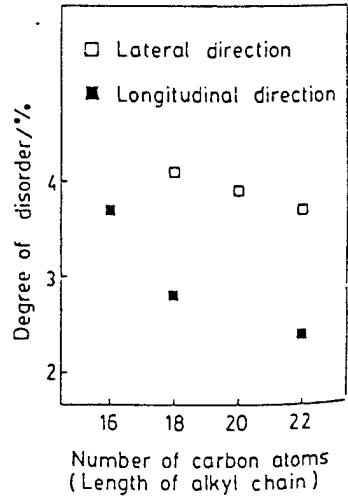


Fig.1.  $D_{lat}$  and  $D_{long}$  for LB films with different alkyl Chain length

also decreased with increasing the alkyl chain length, indicating that an increase of the intermolecular force causes more perfect interlayer regularity along the longitudinal direction in LB film. It is, therefore, considered that the longitudinal regularity in LB films is always followed by the lateral one.

Figure 2 shows the magnitude of  $D_{lat}$  and  $D_{long}$  for the  $2C_{18}Ba$  LB films prepared at 15, 25, and 40  $mN \cdot m^{-1}$ , respectively, as well as the morphological appearance of the monolayer. The magnitude of  $D_{lat}$  increased with increasing the surface pressure. We reported existences of crystalline monolayer domains at the surface pressure of 0  $mN \cdot m^{-1}$ , of a homogeneous monodomain monolayer at 25  $mN \cdot m^{-1}$  and also, of patchy morphology on the homogeneous flat monolayer due to local collapse of monolayer at 40  $mN \cdot m^{-1}$ . Thus, the apparent homogenizing of the monolayer surface with increasing the surface pressure up to 25  $mN \cdot m^{-1}$  does not influence the regularity of the crystalline phase in the LB film. On the other hand, the magnitude of  $D_{long}$  decreased with increasing the surface pressure up to 25  $mN \cdot m^{-1}$ , and then, increased again at 40  $mN \cdot m^{-1}$ . That is, the degree of the interlayer regularity(along the longitudinal direction in LB films) increases with increasing the morphological homogeneity of monolayers.

In conclusion, to obtain the LB film with ordered molecular aggregation along the lateral and longitudinal directions, the monolayer of the amphiphiles with a larger intermolecular aggregation force has to be deposited onto the substrate at the surface pressure where the monolayer surface is homogeneous.

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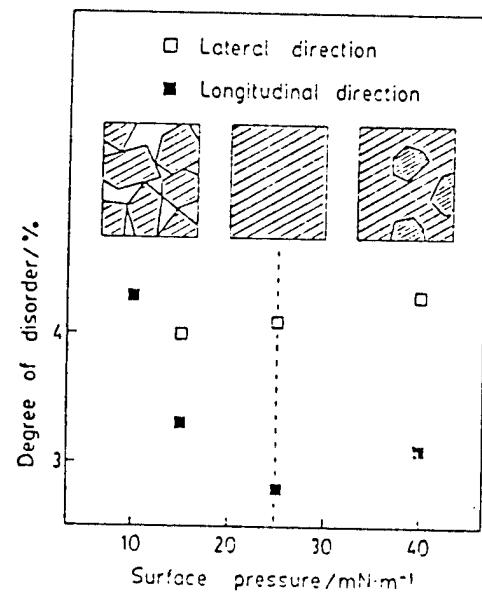


Fig.2.  $D_{lat}$  and  $D_{long}$  for  $2C_{18}Ba$  LB films at different surface pressures

## Determination of Thickness Distribution of a Langmuir-Blodgett Film with Soft X-Ray Reflection

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In preparing a Langmuir-Blodgett film, it is often observed that the deposition ratio at the upward passages decreases gradually, which is known as the XY-type deposition. This phenomenon with an XY-type film relates directly to the deposition mechanism of monolayers onto a solid substrate, and is crucial in obtaining a well-organized film. Though several models have been proposed to explain the XY-type deposition, this phenomenon has not yet been elucidated. Each model suggests a different structure for the XY-type film. Therefore one can determine which model is appropriate with studies of the structure.

We measured the thickness and its distribution of an XY-type film of cadmium arachidate using synchrotron radiation (5nm~10nm). Our method was to measure the wave-length or grazing-angle dependence of the reflectivity and then to analyze the oscillation in its profile due to interference. If a film has a thickness distribution, the observed oscillation is a superposition of oscillations corresponding to various thicknesses (or numbers of layers). Hence we can obtain the distribution by curve-fitting of our experimental results, varying the distribution ratio as a parameter. Fig.1 shows the mea-

surement of the wave-length dependence (●) and its fitting-curve (—) with the XY-type film of cadmium arachidate. Though this film was deposited 71 times, which corresponds to 71 layers, our measurements showed the number of layers to be 53 on average.

This discrepancy in the number of layers (thickness) can be explained only by the Honig's model<sup>1</sup>, which takes account of molecular overturning. As to the thickness distribution, we have simulated his deposition process layer by layer. The simulated thickness distribution agreed with our measurements, and thus we have concluded that his model is the most appropriate one.

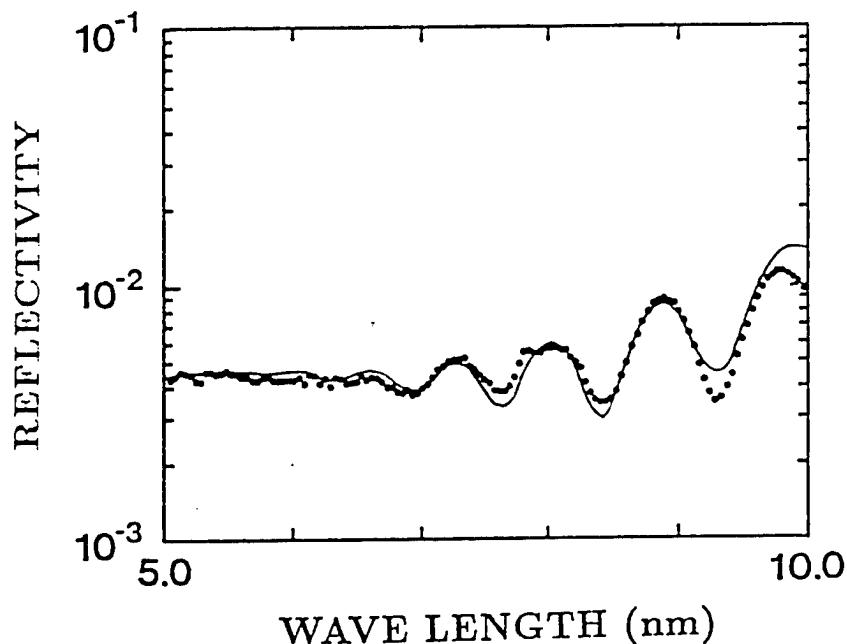


Fig.1

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<sup>1</sup>E. P. Honig, J. Colloid Interface Sci. 43, 66 (1973)

Dependence of Incident Light Angle for Polarized Surface Enhanced  
Resonance Raman Spectra of Langmuir-Blodgett Monolayer Film

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Surface enhanced resonance Raman scattering (SERRS) from a Langmuir-Blodgett monolayer of 4'-n-octylazobenzene-4-oxybutyric acid (AZ396) on rough silver surfaces has been observed in Kretschmann's attenuated total reflection (ATR) configuration (Fig.1).

Figures 2 (a) and (b) show the SERRS spectrum of an LB monolayer of AZ 396 and the Raman spectrum of powdered AZ396, respectively. No significant difference in vibrational frequencies and relative intensities was found between the Raman and SERRS spectra, suggesting that not only the conformation of AZ396 in an LB monolayer does not differ much from that in the powder form but also the interaction between the surface metal and the azo chromophore is weak. These observed peaks relate to the vibration mode of the azo chromophore. No further peaks were detected in the range from 300 to 4000  $\text{cm}^{-1}$ . These results show that the spectra are affected by the enhancement due to resonance Raman scattering. The dependence of SERRS intensity upon the polarization of the excitation laser and its incident angle is shown in Fig.3. According to the calculation by using the Fresnel formula<sup>(1)</sup>, the electric field generation on the Ag surface in the ATR configuration has both horizontal and vertical components. As shown in Figure 3, experimental results are in good agreement with the electric field strengths of horizontal component. This shows that only the horizontal

electric field has influence on the enhancement of the Raman signal. Since surface plasmon polaritons (SPPs) produce only a vertical electric field, the above enhancement effect can not be explained by the effect of SPPs. In conclusion, our results can consistently be explained by considering not SPPs but a short-range electromagnetic field, which is concerned with horizontal electric field, arising at the rough Ag surface.

This study was performed through Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

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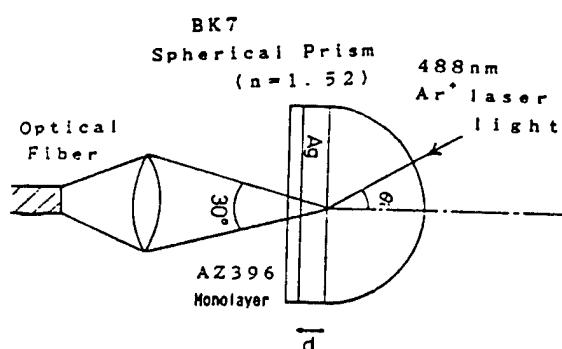


Fig.1 Setup of Raman measurement

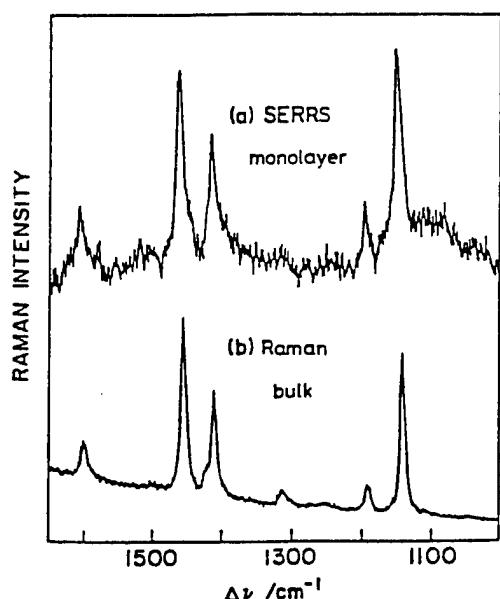


Fig.2 (a) SERRS of AZ396 LB monolayer  
 (b) Raman spectrum of bulk AZ396

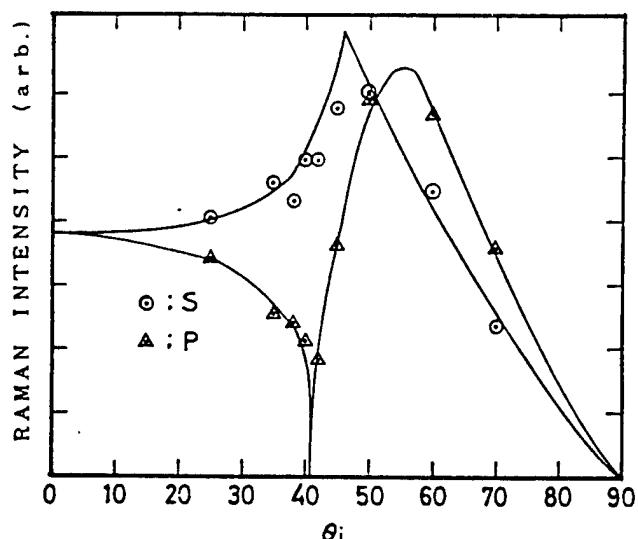


Fig.3 Dependence SERRS of intensity ( $1460\text{ cm}^{-1}$  band) on P and S polarizations of excitation laser and its incident angle

Solid curves are the electric field strengths of horizontal components, which are obtained from the calculation based on Fresnel formula.

Control of Aggregated Structures in Monolayers and Multilayers by Mixing in Molecular Level of Two Azobenzene-Linked Amphiphiles

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The present study was planned to examine the possibility of molecular design and control of miscibility in monolayers at the air-water interface. We will report that two types of molecular level mixing with two amphiphiles in monolayers was realized.

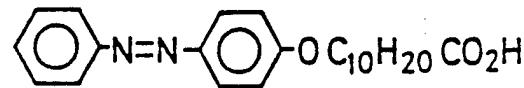
1) Mixed monolayer of two azobenzene-linked amphiphiles with different geometrical shapes.

Two azobenzene-linked amphiphiles,  $\text{AzoC}_{10}\text{COOH}$  and  $\text{C}_{10}\text{AzoCOOH}$  were prepared. The cross section of azobenzene chromophore is much larger than that of aliphatic chain and the axial length of the chromophore well corresponds with the length of 10 methylene sequences.

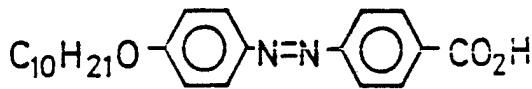
The absorption spectra of  $\text{AzoC}_{10}\text{COOH}$ ,  $\text{C}_{10}\text{AzoCOOH}$  and the mixed monolayers were measured. In the spectrum of the mixed monolayer, the peaks due to component monolayers disappeared and a new peak appeared (Fig. 1). It was demonstrated that the aggregate state in the mixed monolayer was different from those in each component monolayer, and that molecular level mixing in the mixed monolayer was realized (Fig. 2).

2) Mixed monolayer of two similar amphiphiles with different hydrophilic groups.

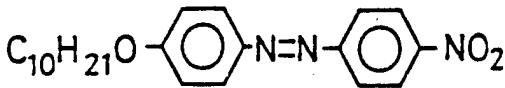
Amphiphiles of  $\text{C}_{10}\text{AzoNO}_2$  do not form a well-behaved condensed monolayer, owing to strong repulsion between the polar molecules. A less polar amphiphile  $\text{C}_{10}\text{AzoCOOH}$ , which possesses the same chemical structure as  $\text{C}_{10}\text{AzoNO}_2$  except for the hydro-



$\text{AzoC}_{10}\text{COOH}$



$\text{C}_{10}\text{AzoCOOH}$



$\text{C}_{10}\text{AzoNO}_2$

philic head, gives a monolayer with a well-defined H-aggregates structure.

The absorption spectra of  $C_{10}\text{AzoNO}_2$ ,  $C_{10}\text{AzoCOOH}$  and the mixed monolayers were investigated. The spectrum of the mixed monolayer looked similar to that of  $C_{10}\text{AzoCOOH}$ . It should be assumed that complete solubility of  $C_{10}\text{AzoNO}_2$  into  $C_{10}\text{AzoCOOH}$  was attained, and that both components took the same aggregation structure as that of monolayer  $C_{10}\text{AzoCOOH}$  as shown in Fig.3. In other words, both amphiphiles oriented nearly normal to the film plane and formed the H-aggregation.

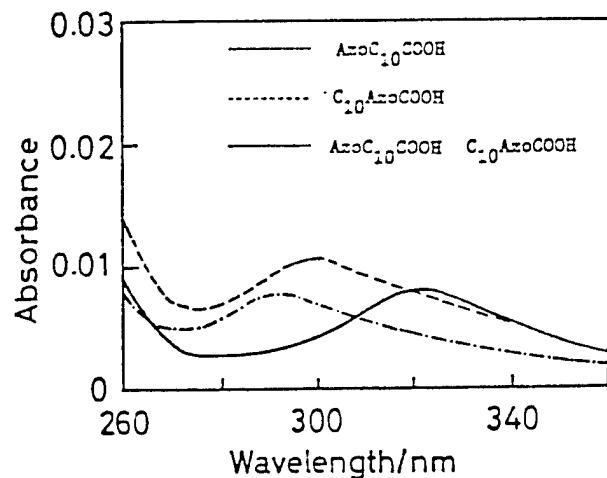


Fig.1 Absorption spectra of the monolayers at the air-water interface. The subphase is an aqueous  $\text{BaCl}_2$  solution,  $M=2 \times 10^{-4}$ ,  $T=18-20^\circ\text{C}$ .

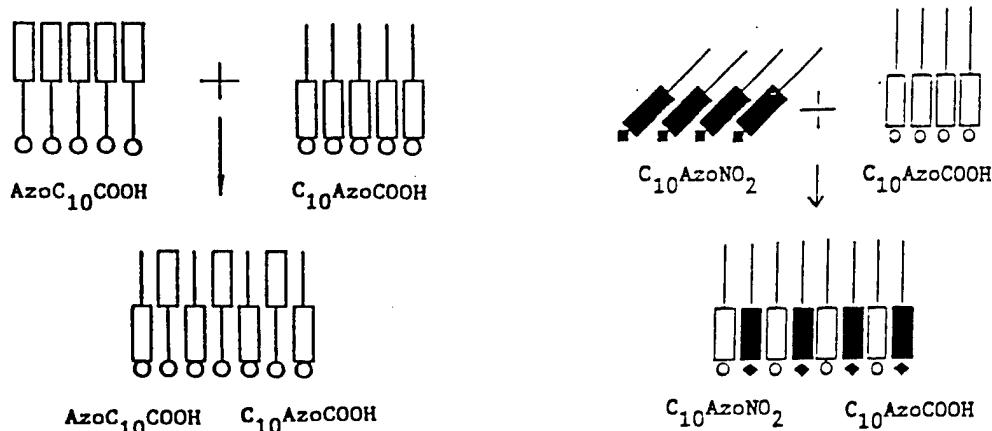


Fig.2 The mixing model of  $\text{Azoc}_{10}\text{COOH}$  and  $\text{C}_{10}\text{AzoCOOH}$ .

Fig.3 The mixing model of  $\text{C}_{10}\text{AzoNO}_2$  and  $\text{C}_{10}\text{AzoCOOH}$ .

J-Aggregate Formation of Long-chain Merocyanine Dye  
in Various Mixed Monolayers and its Exciton Behaviors  
in Langmuir-Blodgett Films.

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Previously, we reported J-aggregates of long-chain merocyanine dyes in the mono- and multilayers mixed with cadmium arachidate (AA) and methyl arachidate<sup>1,2</sup>. In this work, using another long-chain merocyanine (MC) substituted with chlorine (Fig.1) we have examined the J-aggregate formation in the mono- and multilayers mixed with AA, and various lipids such as monostearin (MS), distearin (DS), tristearin (TS), dipalmitoyl-phosphatidylcholine (PC), phosphatidylethanolamine (PE) and cholesterol (Ch). From measurements of visible absorption spectra, different abilities of J-aggregate formation in the mixed LB films have been observed depending on the matrix agents and the compositions. In the cases of mixing of MC with the matrix agents in the molar ratios of 1/1 - 1/5, a sharp absorption band appears at the longer wavelength compared with the monomer band (520nm), except for the mixtures with DS and TS, as shown in Fig.2. These J-aggregates exhibit a red fluorescence by irradiation of green light. Various morphologies of the J-aggregates have been found depending on the matrix agents by fluorescence microscopy.

The exciton-phonon interaction in the J-aggregates has been discussed by applying the Urbach rule to temperature dependence of the absorption spectra. Linear relation-

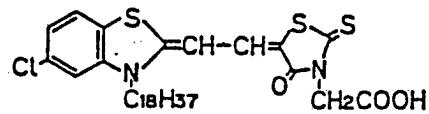


Fig.1. 5-Cl Merocyanine(MC)

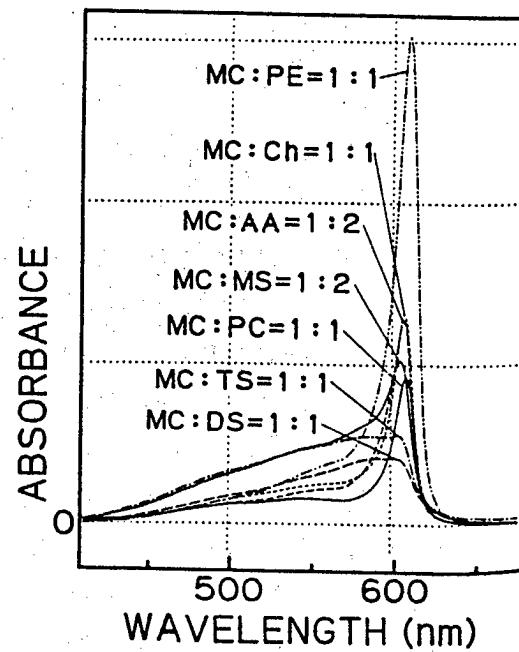


Fig.2. Absorption spectra of LBfilms with J-aggregate

ships between the logarithmic absorption coefficients and the incident photon energy were obtained for the low-energy tail of the J-bands. Provided a steepness index  $S=1.24$  for the two-dimensional system<sup>3)</sup>, it has been found that the exciton-phonon coupling is weak and the fluorescence is radiative annihilation from the free exciton state.

Fig.3 shows the fluorescence decay curve for the J-aggregate LB film of MC/AA = 1/2 measured with a time-correlated single-photon counting apparatus equipped with a picosecond laser system. Two components of the lifetimes fitting to exponential terms were observed to be about 40 ps and 230 ps. Both were prolonged with increasing the AA content. In addition, the decay of fluorescence at 570 nm was slow in contrast to that of J-aggregates. Fig.4 shows the time-resolved fluorescence spectra for the J-aggregate LB film of MC/AA = 1/10. The fluorescence band (610 nm) due to the J-aggregate decreases with time and disappears after about 600 ps, while the 570 nm band is grown up. For the J-aggregate LB films of pure MC or MC/AA = 1/2, the rise of 570 nm band was markedly delayed.

In systems of the J-aggregate as a donor combined with an acceptor layer at a distance of 20.2 - 30.2 Å, the fluorescence of the J-aggregate decayed more rapidly.

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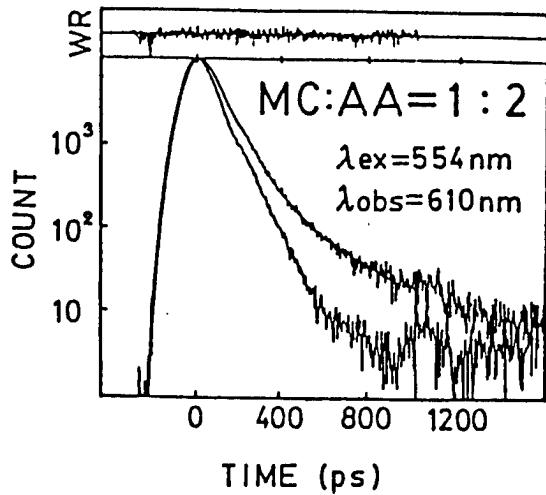


Fig.3. Fluorescence decay curve of J-aggregate LB film

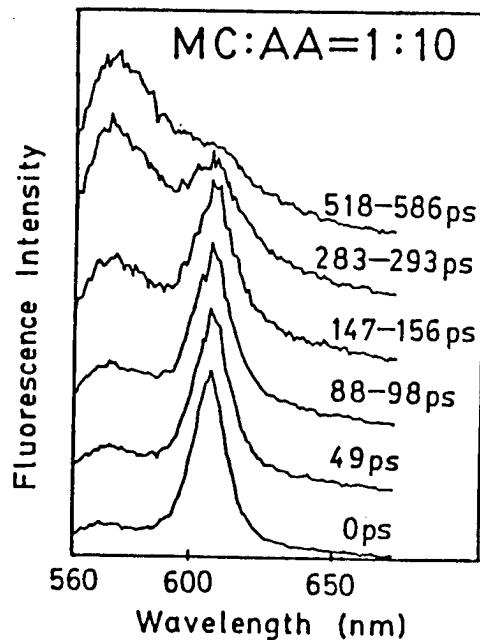


Fig.4. Time-resolved fluorescence spectra of J-aggregate LB film

**Correlation between ESR and Optical Anisotropy in Langmuir-Blodgett Films of a Merocyanine Dye**

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The existence of stable radical species has been demonstrated in the mixed Langmuir-Blodgett films of a merocyanine dye, having benzothiazole as a donor nucleus, and arachidic acid [1]. The computer analysis of the anisotropic spectral line shape, with clear nitrogen hyperfine structure for the in-plane spectra, has determined the angular distribution function of the radical molecules [2]. The results suggest that the radicals are associated with J-aggregates, which are aligned along the dipping direction of the substrate due to the flow orientation.

Recent theoretical analysis of the flow orientation of molecular domains during the monolayer transfer process has successfully explained the observed in-plane distribution function of the radical molecules and also the optical dichroism in the film plane [3].

The theory further predicts that the degree of molecular orientation is dependent on the dipping velocity  $v_d$ , the width of substrate  $a$ , and the substrate position  $x(-a/2 \leq x \leq a/2)$ , due to the variation of flow forces. While this effect has been confirmed for the majority of dye molecules forming J-aggregate by optical measurements [4], the same effect should be observed for the radical molecules, if they are associated with J-aggregates as proposed. We report the ESR spectra in the samples prepared with different values of  $a$  and  $v_d$  and discuss the orientation of radicals.

The angular distribution function of the molecules in the film plane is represented by the form [2-4],

$$P(\theta) \propto \exp(-\sin^2(\theta \pm \theta_0)/2\sin^2\delta). \quad (1)$$

$\theta$  denotes the angle between the  $p\pi$  orbital axis and the dipping direction.  $\pm\theta_0$  show the most probable orientation. The molecules show a characteristic orientation of  $\theta_0 \approx 60^\circ$ .  $\delta$  shows the width of distribution and is defined as follows:

$$1/2\sin^2\delta = \zeta G/k_B T. \quad (2)$$

The local stress  $\zeta G$  is given as a sum of two terms, assuming a Bingham fluid, considering the plasticity of the monolayer.

$$\zeta G = \zeta' (4/\pi)(v_d/a)(1-4x^2/a^2)^{-1} + f. \quad (3)$$

$\zeta'$  shows a Newtonian friction coefficient and  $f$  shows a Bingham yield value. The dependence of the orientation on the above mentioned parameters originates from the first term in eq.(3). The higher degree of orientation is expected for the higher dipping velocity or the narrower substrate-width and toward the edge of substrate. The relative intensity of the resolved triplet hyperfine structure due to a nitrogen nucleus in the observed ESR spectra yielded the orientation of radicals, qualitatively consistent with the theoretical prediction. The coincidence supports the proposed origin of radicals.

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Photopolymerization in Langmuir-Blodgett film of an amphiphilic cyclodextrin derivative containing a diacetylene group

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Previously we reported reversible cis-trans isomerization of azobenzenes included in the Langmuir-Blodgett (LB) films of amphiphilic alkylamino-cyclodextrins(CnN-CDs).<sup>1,2)</sup> It has been found that the cavity in CnN-CDs offers a favorable environment for the isomerization in the host-guest LB film and will provide various possibilities of control of the photochemical reactions. The long alkyl chain of CnN-CDs is essential for preparing LB film, whereas it is dispensable part for special properties such as optical and electronic properties. We intend to introduce diacetylene group into the long alkyl chain, expecting the further extended investigation as follows;

- (i) study on interactions between the polydiacetylene in the alkyl group and a guest molecule in the cavity,
- (ii) study on immobilization by intermolecular subsequent polymerization with UV irradiation because the monomer has seven photoreactive sites of diacetylene moiety.

This amphiphile, heptakis(6-(tricosanoate)-12'-diynyl-carbamoyl)-6-deoxy)-2,3-di-O-methyl- $\beta$ -cyclodextrin (Diace-BCD; molecular weight: 3624), was synthesized in a similar manner as reported in the previous paper,<sup>3)</sup> and is highly soluble in cyclohexane, chloroform, and tetrahydrofuran (THF). The limiting area of the monolayer is about  $3.0 \text{ nm}^2$  on water (Fig.1). The LB films were deposited as Y-type multilayers on a quartz plate precoated with five monolayers of cadmium eicosanoate.

After the exposure with a low-pressure Hg lamp ( $1 \text{ mW/cm}^2$ ) in nitrogen atmosphere (irradiation time: > 3 min), the irradiated multilayers were colored (gold) and became insoluble in THF. By

means of gel permeation chromatographic analysis, it was found that oligomers within tetramer was soluble in THF. Therefore, a high-molecular-weight polymer formed in the LB film. Figure 2 shows the change in electronic absorption spectra with the increase of exposure time to the LB film. The absorption bands near 250 nm increased on the irradiation with 254 nm light, while the bands corresponding to polydiacetylene were not appeared in visible region. Consequently, we found the polymerization of diacetylene groups, in other words, the fixation of Diace- $\beta$ CD in the LB film.

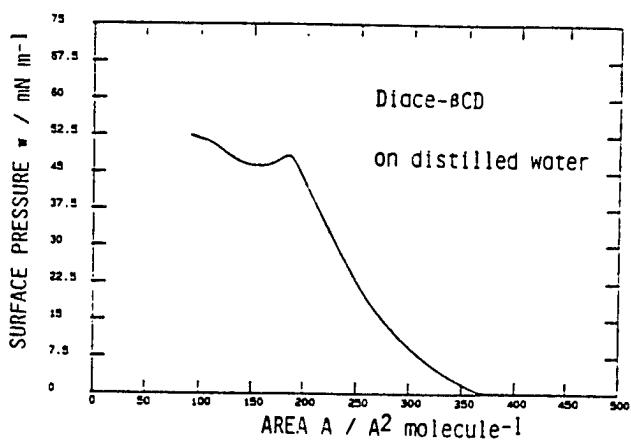
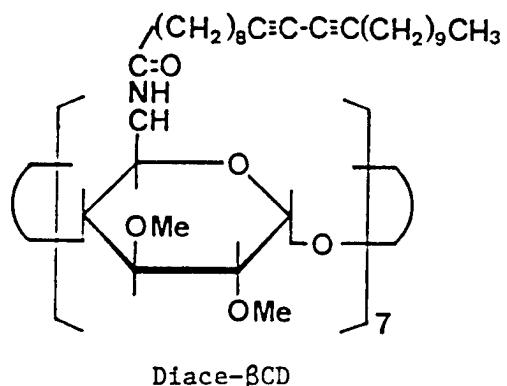


Fig.1 Surface pressure-area isotherms for the monolayer of Diace- $\beta$ CD

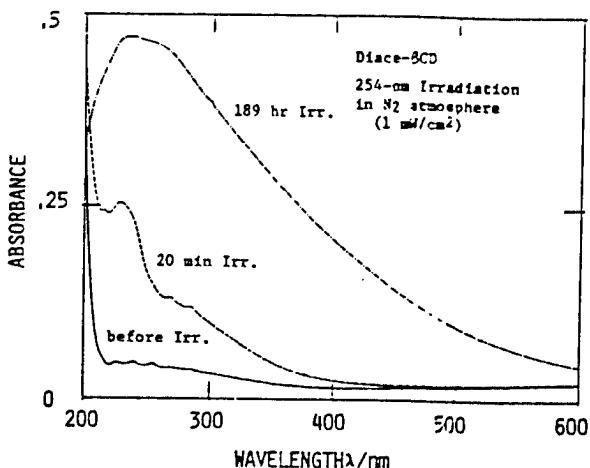


Fig.2 UV-Vis absorption spectra for the LB film Diace- $\beta$ CD before and after irradiation

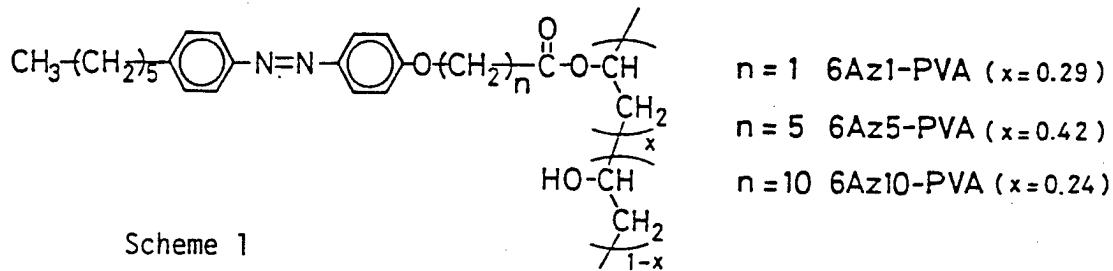
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**Formation and Langmuir-Blodgett Deposition of Monolayers of Poly(vinyl alcohol) Bearing Azobenzene Side Chains.**

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**Introduction** Studies on reaction behaviors of cis/trans thermal and photoisomerization (photochromism) of azobenzene in LB films are limited because of their poor reactivity in these restricted environments.<sup>1</sup> Recently reactive azobenzene LB films have been proposed by two Japanese groups. These films consist of amphiphilic cyclodextrins including azobenzene derivatives<sup>2</sup> and azobenzene amphiphiles complexed with polyelectrolytes.<sup>3</sup> In this paper, a new type of photochromic LB films is reported which are composed of poly(vinyl alcohol)s (PVA) having pendant azobenzene units<sup>4</sup> (6Azn-PVA, Scheme 1). These films are applicable to "command surfaces" which control alignment of nematic liquid crystals, and this will also be presented in this conference.<sup>5</sup>



**Experimental** 6Azn-PVA were synthesized by ester formation between PVA and carboxylic acid derivatives of azobenzene amphiphiles. Degree of esterification was determined spectrophotometrically and shown in the scheme. A Lauda film balance was used for measurements of the surface pressure and transfer of monolayers onto substrates.

**Results and Discussion** Figure 1 shows the surface pressure-area (per azobenzene (Az) unit) isotherms ( $\pi$ -A curves) of 6Azn-PVA spread in the trans (a) and cis (b) form. In the trans form,

the difference of the methylene spacer length made little effect on the  $\pi$ -A curve, the limiting area per unit ranging 0.31-0.38 nm<sup>2</sup>. On the other hand, the monolayers spread in the cis form gave quite different shape in the  $\pi$ -A curve which was largely dependent on the spacer length. This can be reasonably understood by assuming contact of polar cis Az units with the water subphase.

The monolayers could be readily transferred to a quartz substrate both in the trans and cis forms. Figure 2 shows u.v.-visible absorption spectra of deposited trans and cis 6Az1-PVA monolayer films on a quartz plate with perpendicular incidence. Efficient and reversible isomerization occurred in the LB films, particularly in the film deposited in the cis form. Probably suppression of Az aggregation brought about by the disturbance of PVA backbone is responsible for this high reactivity.

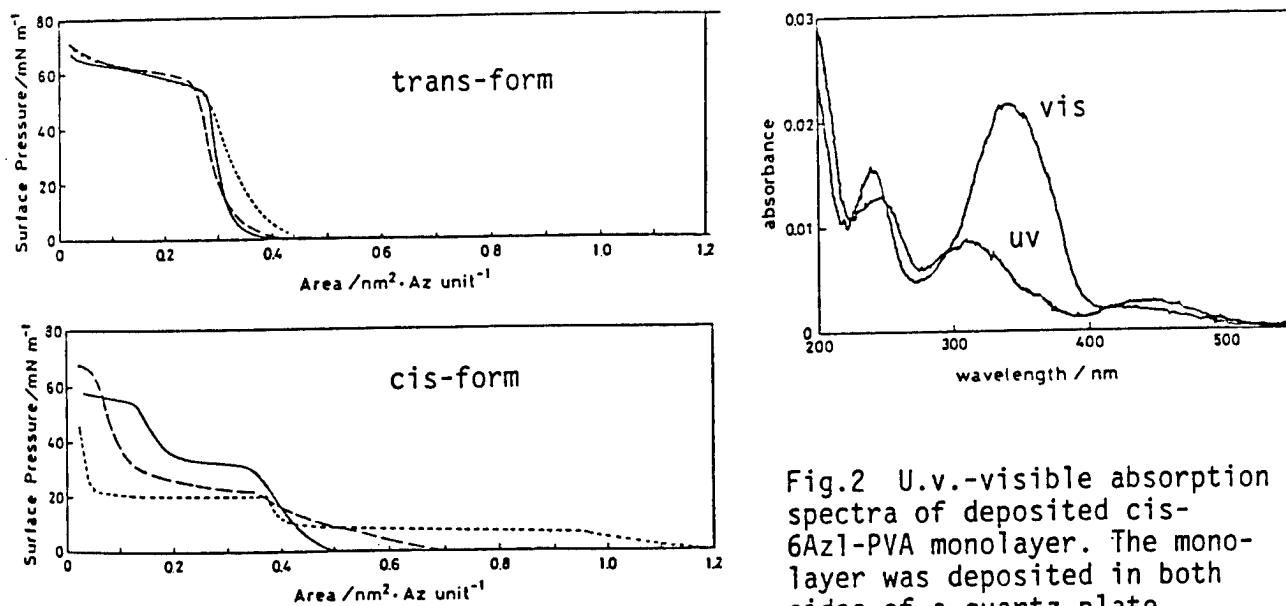


Fig.2 U.v.-visible absorption spectra of deposited cis-6Az1-PVA monolayer. The monolayer was deposited in both sides of a quartz plate.

Fig.1  $\pi$ -A isotherms of monolayers of 6Azn-PVA on distilled water at 21 °C.  
n=1(—); 5(---); 10(- - -).

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Preparation of Multilayers  
using Chemical Adsorption and Electron-Beam Irradiation

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Multilayers of  $\omega$ -nonadecenyl-trichlorosilane (V-NTS:  $\text{CH}_2=\text{CH}-(\text{CH}_2)_{17}-\text{SiCl}_3$ ) have been prepared on  $\text{SiO}_2/\text{Si}$  substrate by repeated cycle of chemical adsorption (CA) method and electron beam (EB) irradiation. (Fig.1) The CA process was carried out in a nonaqueous solvent resolved V-NTS at various temperatures. The procedure was already reported by L. Netzer et al.<sup>1)</sup> The EB irradiation was carried out in air, helium, oxygen or nitrogen atmosphere.

Molecular density and molecular arrangement of the multilayers were measured by multiple external reflection (MER) FTIR spectroscopy. (Fig.2) The FTIR spectroscopy has been proved to be effective in obtaining IR spectra of extremely thin organic films<sup>2)</sup>. The molecular density of V-NTS monolayer of the highest density was higher than that of  $\omega$ -tricosenoic acid ( $\omega$ -TSA:  $\text{CH}_2=\text{CH}-(\text{CH}_2)_{20}-\text{COOH}$ ) monolayer built-up by LB method, and pin-hole density of the film was lower.

Vinyl group of V-NTS disappeared and hydroxyl, aldehyde, and/or carboxyl groups seemed to be formed when the irradiation was carried out in oxygen atmosphere, while imino and/or amino group seemed to be formed instead of those groups when the irradiation was carried out in nitrogen atmosphere.

The molecular density or molecular arrangement was controlled by the preparation temperature and the EB irradiation dose. (Fig.3)

Thickness of the multilayers was measured by ellipsometry. The thickness was increased by fixed value at every CA process. Using this method, multilayers of high molecular-density can be obtained easily. (Fig.4)

This method may be useful for the preparation of organic ultrathin films such as coating films for an optical fiber, lubricant for a magnetic recording media, and dielectric films for a condenser, and, further, be employed for selective chemical adsorption for building-up molecular structures such as molecular devices by using selective EB irradiations.

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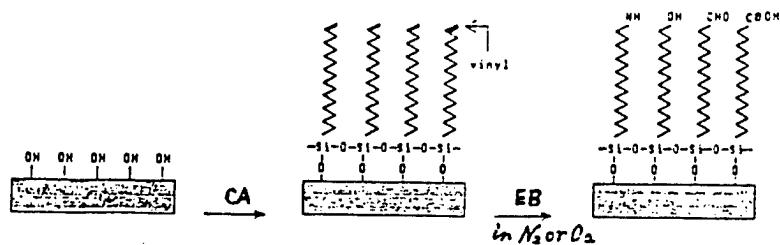


Fig.1 Schematic view of the chemical adsorption and the EB irradiation process.

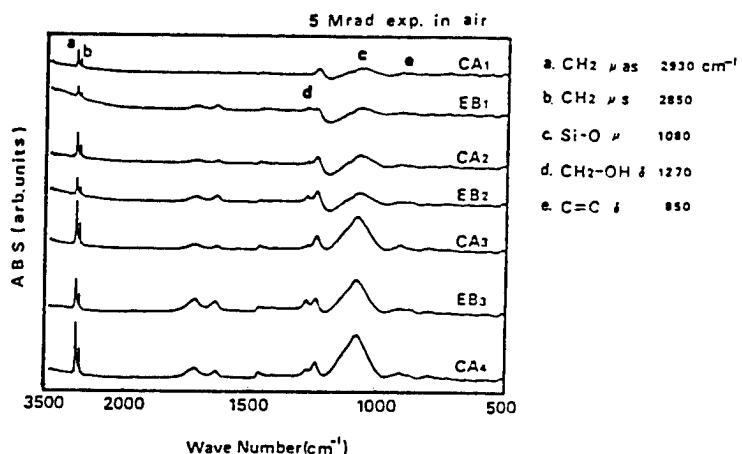


Fig.2 IR spectra of a CA monolayer and CA multilayers.

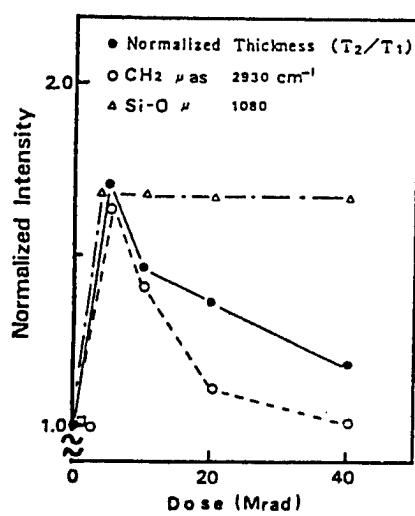


Fig.3 IR intensity changes of CA monolayers as a function of EB irradiation dose.

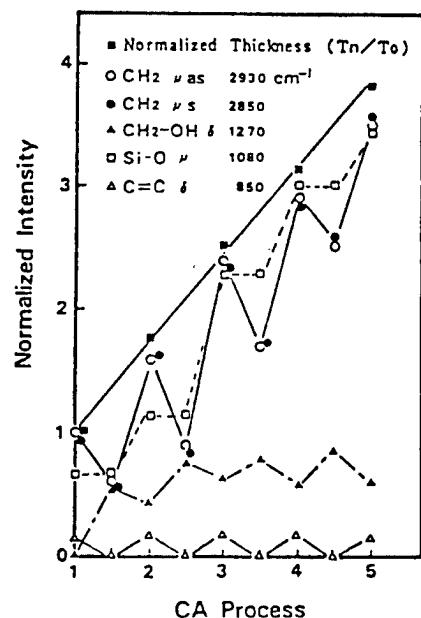


Fig.4 IR intensity and thickness changes of CA multilayers at every CA process.

Electrocatalytic Reduction of CO<sub>2</sub> on Modified Electrode with  
Alkyl Cyclam-Metal Complex LB Films.

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In biological systems, various kinds of metal complexes such as hemes, iron sulfur clusters, and manganese centers act as active sites of enzymes. Several recent papers reported that carbon dioxide could be electrocatalytically reduced by metal complexes<sup>1,2)</sup>. The metal electrodes in contact with an aqueous solution of a cyclam-Ni<sup>2+</sup> complex can reduce carbon dioxide to carbon monoxide selectively in more preferable potentials than the same metal electrode without the complex.

To immobilize metal complex catalysts on an electrode, we synthesized two kinds of nickel cyclam derivatives with four or one N-substituted alkyl chains, i.e. tetrakis(N-hexadecyl)-cyclam-Ni<sup>2+</sup> complex (1 in Fig. 1) or N-hexadecylcyclam-Ni<sup>2+</sup> complex (2 in Fig. 1). We examined their monolayer properties and the catalytic activities for reduction of carbon dioxide.

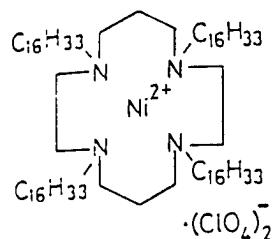
The monolayers of the nickel cyclam derivatives were spread from the chloroform solutions onto 0.5 mM NaClO<sub>4</sub> aqueous solution at 15°C. Fig. 2 shows the  $\pi$ -A isotherms of nickel cyclam derivatives. The monolayers of 1 shows large extended area compared with that of 2. The limiting areas of 1 was smaller than the theoretical value of 0.80 nm<sup>2</sup> estimated for four alkyl chains.

The monolayers of these complexes were deposited on glassy carbon (GC) disk electrodes, and the cyclic voltammograms on these electrodes were recorded in 0.1 M NaClO<sub>4</sub> aqueous solution under the nitrogen or the carbon dioxide atmosphere. As shown in Fig. 3, under carbon dioxide, the increase in cathodic current was observed at the potentials more negative than -1.4 V vs. SCE, compared with that under the nitrogen atmosphere. The increase in the cathodic current disappeared in the solution without carbon dioxide. This results indicate that nickel cyclams with long alkyl chains have catalytic activity for carbon dioxide

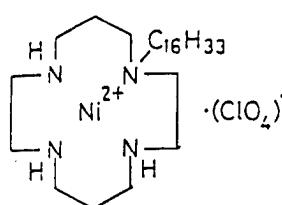
reduction.

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1



2

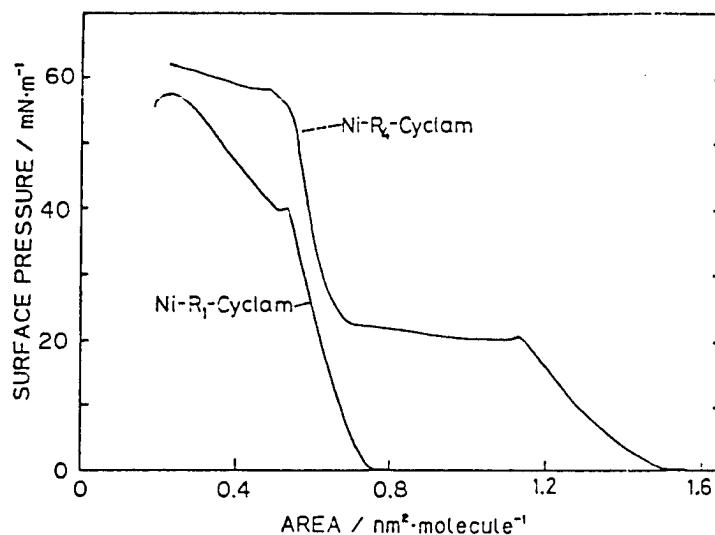


Fig. 1 Nickel cyclams with long alkyl chains synthesized in this work.

Fig. 2  $\pi$ -A isotherms of nickel cyclam derivatives.  
subphase : 0.5 mM  $\text{NaClO}_4$  aqueous solution.

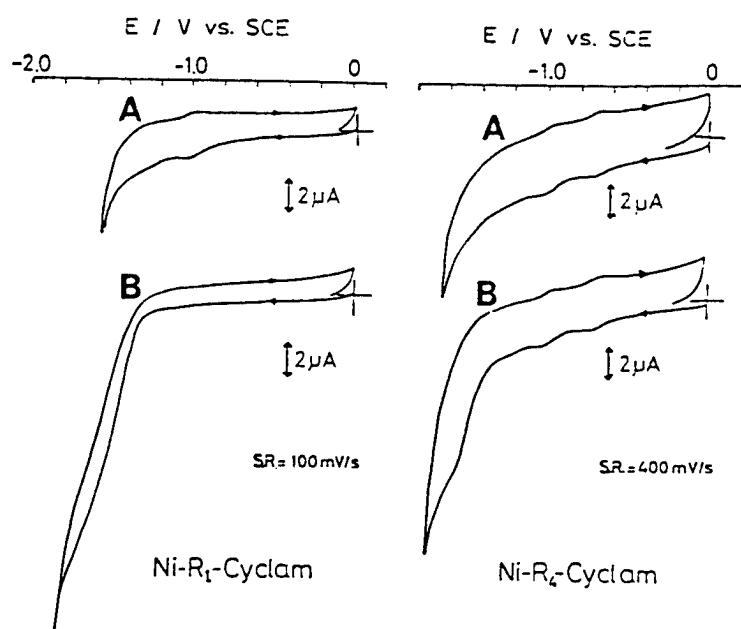


Fig. 3 Cyclic voltammograms on GC electrode coated with nickel cyclam LB films in 0.1 M  $\text{NaClO}_4$  aqueous solution under the atmosphere of (A)  $\text{N}_2$ ; (B)  $\text{CO}_2$ .

# SYNTHESES OF CONDUCTING POLYMER LB MULTILAYERS

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## 1. Introduction

As a promising electronic material, much attention has been recently directed to the conducting polymer LB film. Up to date, there have been some reports<sup>1-9</sup> on this subject. Fig. 1 summarizes the design of conducting polymer LB films in which the polymer backbone lay on each layer.

In this paper, we report and discuss three types of preparative methods of conducting polymer LB multilayers.

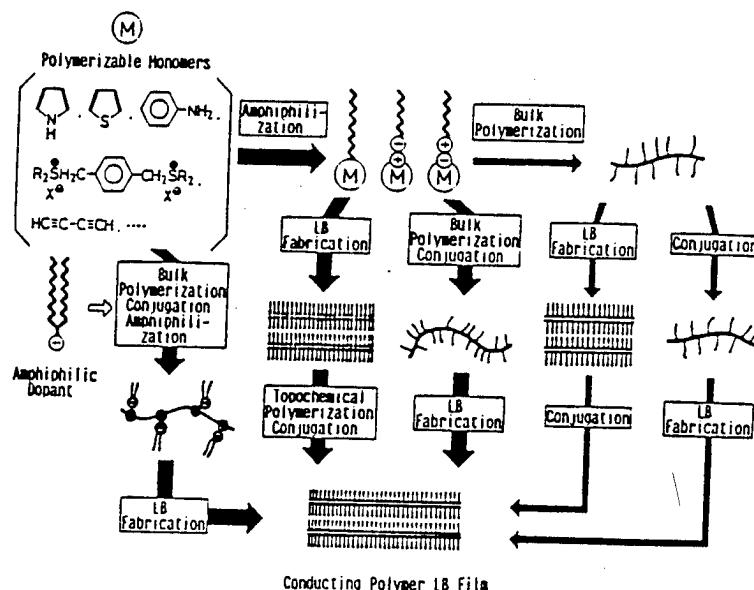


Fig. 1. Design of conducting polymer LB films.

## 2. Conducting Polypyrrole LB Multilayer Prepared by the Electrochemical Polymerization of the Monomeric LB Multilayer<sup>2-4</sup>

The mixture of amphiphilic pyrrole derivative, octadecyl 4-methylpyrrole-3-carboxylate or 4-methyl-1-octadecylpyrrole-3-carboxylic acid, and octadecane formed stable monolayer on pure water. The monomeric multilayers (100-300 layers) on the ITO electrode by the vertical dipping method were converted into polypyrrole (PPy) multilayers by the electrolytic oxidation in  $\text{CH}_3\text{CN}$  containing  $\text{LiClO}_4$ .

The Y-type structure of the multilayers was confirmed by the X-ray diffraction pattern and the TEM picture of the cross section of the films. The PPy LB multilayer had highly anisotropic dc conductivity by ca. 10 orders ( $\sigma_{\parallel} = 10^{-1} \text{ S/cm}$ ,  $\sigma_{\perp} = 10^{-11} \text{ S/cm}$ ), as was speculated from its alternatively layered structure of PPy layers and alkyl chain layers. Furthermore, it was suggested that the ideal contact between the PPy layers and the macro ITO electrode was formed simultaneously on electrolytic polymerization.

## 3. Conducting Polymer LB Multilayer Prepared by the LB Fabrication of Soluble Conducting Polymer

### 3-1. Polyaniline Multilayer Prepared from the Long Alkylated Polyaniline

The amphiphilic long alkylated aniline, 2-octadecoxyaniline ( $C_{18}OAn$ ), was converted into amorphous polymer, poly( $C_{18}OAn$ ), by the bulk chemical oxidation of  $C_{18}OAn$  with  $(NH_4)_2S_2O_8$  in THF and HClaq. mixed solution. Poly( $C_{18}OAn$ ) was soluble in organic solvents whose relative dielectric constants were 2-12, and formed stable monolayer on dil. HCl or pure water.

The multilayers (100-200 layers) on the polyester substrate by the horizontal lifting method were speculated to have X-type structure, which was shown by the X-ray diffraction pattern and the TEM picture of the cross section of the film. After exposure to iodine vapor, the multilayer prepared from dil. HCl subphase had highly anisotropic dc conductivity by ca. 4 orders ( $\sigma_{\parallel}=10^{-6}$  S/cm,  $\sigma_{\perp}=10^{-10}$  S/cm), as was speculated from its alternatively layered structure.

### 3-2. Polypyrrole Multilayer Prepared from the Polypyrrole Derivative with Relatively Short Alkyl Chain

The electrolytic polymerization of pyrrole derivatives includes an in situ doping with anionic species. Preparation of the multilayer of poly(3,4-dibutylpyrrole) (poly(DBP)), whose amphiphilic property was improved by the doping of amphiphilic anionic molecule, was examined.

Poly(DBP) doped with perfluorooctanoic acid (P8) and poly(DBP) doped with trifluoroacetic acid (P2) were prepared by the electrolytic oxidation of 3,4-dibutylpyrrole in  $CH_3CN$  containing perfluoroalkylcarboxylic acids. P2 and P8 were soluble in organic solvents whose relative dielectric constants were 8-35, and formed monolayers on pure water.

The multilayers (50-100 layers) on the polyester substrate by the horizontal lifting method had uniform thicknesses, which were shown in the TEM picture of the cross section of the films. The thickness of the P8 multilayer coincided with that speculated from the CPK molecular model. On the other hand, the thickness of the P2 multilayer was significantly larger than the speculated value. After exposure to iodine vapor, the P8 multilayer had highly anisotropic dc conductivity by ca. 3 orders ( $\sigma_{\parallel}=10^{-6}$  S/cm,  $\sigma_{\perp}=10^{-9}$  S/cm).

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SYNTHESSES OF TETRATHIOFULVALENE DERIVATIVES AND  
PROPERTIES OF THEIR LB FILMS

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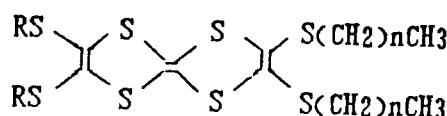
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Although the researches on the application of Langmuir-Blodgett (LB) technique in the area of organic conductor are at their initial stage, the broad properties have been developed, and the success of conductive LB films will lay the foundation for the realization of future molecular devices.

Since the first organic conductor, charge transfer complex (CTC) of tetrathiofulvalene tetracyanoquinodimethane (TTF $\times$ TCNQ), was discovered in the world, a series of TTF derivatives have been synthesized, their structures and physical properties have been studied in detail. Among these compounds the structures and properties of organic superconductors, (BEDT-TTF) $_{213}$  and (TTCn-TTF) $\times$ X have received the most attention. According to the needs suitable for the LB method and the structural feature of two molecules mentioned above, the following asymmetrical TTF derivatives were designed and synthesized.



(1), R=-CH<sub>2</sub>-CH<sub>2</sub>-, n=15

(2), R=-CH<sub>2</sub>-CH<sub>2</sub>-, n=17

(3), R=-CH<sub>3</sub>, n=15

Their 1:1 CTC with tetrafluorotetracyanoquinodimethane (TCNQF<sub>4</sub>) were prepared by mixing equimolar solutions of corresponding donor and acceptor in CH<sub>2</sub>Cl<sub>2</sub>. These compounds were confirmed by their melting points, elemental analyses, IR and <sup>1</sup>H-NMR spectra.

Although TTCn-TTF alone yields unstable monolayers at any surface pressure, they can form very stable monolayers with some amount of arachidic acid (the content of TTCn-TTF ranges from 5 to 50%) and are suitable to build up true LB multilayers.

However, their TCNQF<sub>4</sub> complexes exhibit very good monolayer formation behaviors. The typical surface pressure-area per molecule (F-A) isotherms show that the area occupied by one molecular complex are, (1)\*TCNQF<sub>4</sub>, 90 Å<sup>2</sup>; (2)\*TCNQF<sub>4</sub>, 90.8 Å<sup>2</sup>; (3)\*TCNQF<sub>4</sub>, 83 Å<sup>2</sup>. We choose chloroform as a spreading solvent; nano-pure grade water as subphase; quartz, calcium fluoride, conducting glass as solid substrates. Fifty-layer-thick films were obtained at a constant surface pressure of 35 mN/m.

The conductivity of the LB films at room temperature were measured. The σ<sub>ab</sub> and σ<sub>1ab</sub> of (1)\*TCNQF<sub>4</sub> and (3)\*TCNQF<sub>4</sub> CTC are ca. 1×10<sup>-4</sup> s/cm, 1×10<sup>-7</sup> s/cm, 4×10<sup>-7</sup> s/cm and 1×10<sup>-7</sup> s/cm respectively. Upon iodine vapour doping and a moderate heating treatment at ca. 40 °C for half an hour, the σ<sub>ab</sub> of [(1)\*TCNQF<sub>4</sub>]Ix jumped to ca. 2.5×10<sup>-1</sup> s/cm and the σ<sub>1ab</sub> of [(3)\*TCNQF<sub>4</sub>]Ix jumped to ca. 1×10<sup>-3</sup> s/cm.

The binding energy of S<sub>2p</sub>, C<sub>1s</sub>, F<sub>1s</sub>, N<sub>1s</sub> and I<sub>3d $\frac{5}{2}$</sub>  of the neutral TTCn-TTF derivatives, their TCNQF<sub>4</sub> complexes, LB films and doped I LB films were determined by XPS.

# Electron Spin Resonance Study on Langmuir-Blodgett Films of the Complexes of Alkylammonium and Metal-(dmit)<sub>2</sub> Anion

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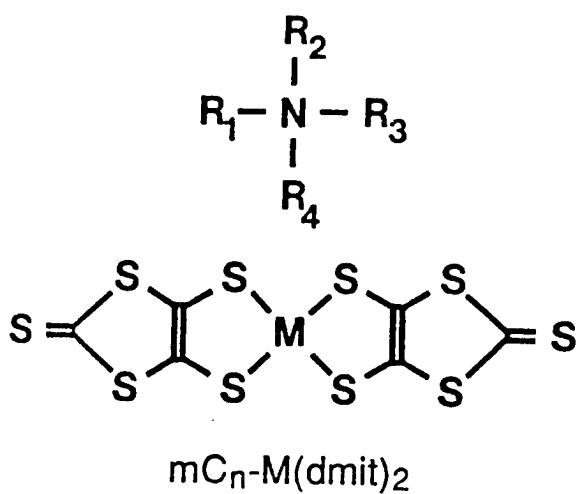
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The complex of transition metal (M) and the sulfur containing ligands, dmit ( $H_2dmit = 4,5\text{-dimerocapto-1,3-dithiol-2-thione}$ ), is known as the electron accepter which forms the superconducting columnar structure. Recently this metal-dmit complex ( $M(dmit)_2$ ) was successfully introduced into Langmuir-Blodgett (LB) film system by using dialkyldimethylammonium ( $2C_n$ ) or trialkylmethylammonium ( $3C_n$ ) as electron donors.<sup>1-3</sup> In particular, the electrochemically oxidized film of  $3C_{10}\text{-Au}(dmit)_2$  was recognized as *the first macroscopically metallic system* with the highest conductivity of 30 S/cm among LB film system.<sup>3)</sup> We performed the electron spin resonance (ESR) study on the LB film samples as well as the powder samples of these complexes,  $mC_n\text{-}M(dmit)_2$  (Fig.1). Following features have been obtained for the precursor systems before oxidation.

A characteristic ESR signal (Fig. 2) was obtained for a powder sample of  $3C_{10}\text{-Au}(dmit)_2$ . The estimated spin density was  $0.7 \times 10^{-3}$  spin/complex at room temperature. The spin susceptibility increases with decreasing temperature down to 20 K and takes a maximum at that temperature. The ESR spectrum observed in an LB film of  $3C_{10}\text{-Au}(dmit)_2$  also has a structure, but it was much narrower than that for the powder sample mentioned above, and showed a clear anisotropy. The estimated spin susceptibility was  $3 \times 10^{-2}$  spin/complex, 4 times as large as that of the powder sample. The temperature at which the spin susceptibility of the LB film system takes its maximum was the same as that for the powder sample, 20 K, suggesting that the radical spins in the LB system retain their physical properties in the powder sample to a certain extent.

In the powder sample of  $2C_{10}\text{-Ni(dmit)}_2$ , a structureless and symmetrical signal was observed. Its peak to peak linewidth was about 180 gauss and the estimated spin density was about 1 spin/complex. On the contrary, the line shape obtained for an LB film of  $2C_{18}\text{-Ni(dmit)}_2$  had a structure and showed a large anisotropy. The peak to peak linewidth with the external magnetic field normal to the plane was only about 5 gauss and the estimated spin density was of the order of  $10^{-1}$  spin/complex. These facts suggest the strong correlation between the radical spins in LB film samples.

The ESR spectra of these systems are clearly dependent on the central metal species and the number of the alkyl chains as expected. The results for oxidized samples will be also presented at the conference.



$m=2$ :  $R_1=R_2=C_nH_{2n+1}$ ,  $R_3=R_4=CH_3$   
 $m=3$ :  $R_1=R_2=R_3=C_nH_{2n+1}$ ,  $R_4=CH_3$   
 $M=\text{Au or Ni}$

Fig. 1 Chemical structure of  $mC_n\text{-M(dmit)}_2$ .

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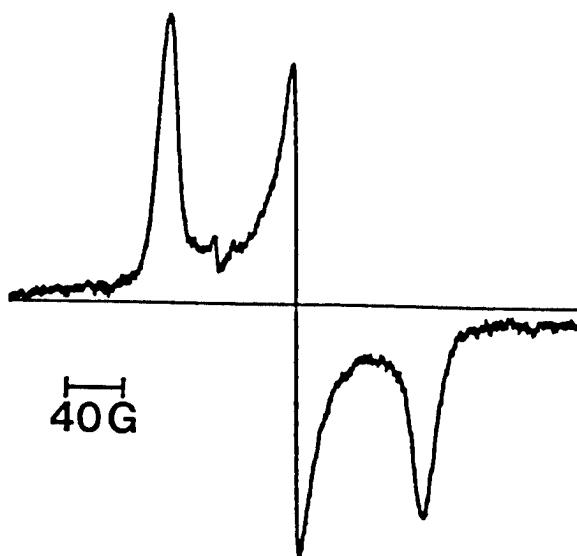


Fig. 2 The ESR spectrum observed for a powder sample of  $3C_{10}\text{-Au(dmit)}_2$  at room temperature.

Electric and Spectroscopic Properties of  
Langmuir-Blodgett Films Containing Tetracyanoquinodimethane  
with Various Mixed Valent States

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Langmuir-Blodgett (LB) films of amphiphiles containing mixed valent tetracyanoquinodimethane (TCNQ) are known to show high electric conductivity.<sup>1)</sup> Such conductivity is expected to depend on the mixed valent states and the molecular arrangement of TCNQ in the LB films. In this work, we report the electric conductivities, the electron spin resonance (ESR) spectra, and the electronic spectra of the LB films and cast films of several amphiphiles containing TCNQ (octadecyl TCNQ ( $C_{18}$ TCNQ)), N-octadecylpyridinium TCNQ salts ( $C_{18}$ Py-(TCNQ)<sub>n</sub>), and N-docosylpyridinium TCNQ salts ( $C_{22}$ Py-(TCNQ)<sub>n</sub>), n=1,2) with various mixed valent states.

The mixed valent states of TCNQ [ $(TCNQ^-)_x(TCNQ)^{1-x}$ ] in these LB films was controlled electrochemically by the controlled potential electrolysis or chemically by mixing two TCNQ amphiphiles with different mixed valent states. The conductivities of LB films and cast films deposited on patterned Au micro-electrodes (Fig. 1) were determined from the slope of i-V curves observed when triangular waves were applied between two Au microelectrodes.

The mixed LB films of  $C_{18}$ TCNQ with methylarachidate (AME) (1:1) deposited on  $SnO_2$  coated glass substrates were electro-chemically reduced at constant electrode potential, and then the ESR spectra of the mixed LB films were measured.

The conductivities of LB films and cast films prepared in various conditions are listed in Table 1. The conductivity of the electrochemically reduced mixed LB films of  $C_{18}$ TCNQ with AME (1:1) have maximum value at -0.10 V vs. SCE which corresponds to the reduction potential ( $TCNQ^{0/-1}$ ) of the mixed LB films of  $C_{18}$ TCNQ. The conductivity of the mixed cast film of  $C_{22}$ Py-TCNQ and  $C_{22}$ Py-(TCNQ)<sub>2</sub> increased drastically with the content of  $C_{22}$ Py-(TCNQ)<sub>2</sub>.

Figure 2 shows the dependence of the peak to peak line width ( $\Delta H_{pp}$ ) of the ESR spectrum of the mixed LB films of  $C_{18}$ TCNQ with AME (1:1) on the angle ( $\theta$ ) between the direction of the static magnetic field and that normal to the film. The  $\Delta H_{pp}$  for the mixed LB film has the smallest value at 0 V vs. SCE which is near the reduction potential of the mixed LB film. The dependence of  $\Delta H_{pp}$  on  $\theta$  shown in Fig. 2 and their temperature dependence are different from that for the LB film of  $C_{22}$ Py-(TCNQ)<sub>2</sub><sup>2)</sup>.

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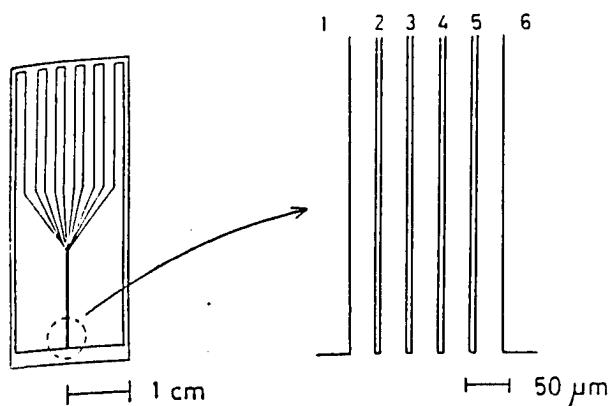


Fig. 1 Patterned Au electrodes fabricated on quartz slide glass. Small Au electrodes were 10  $\mu\text{m}$  wide and separated by 30  $\mu\text{m}$ .

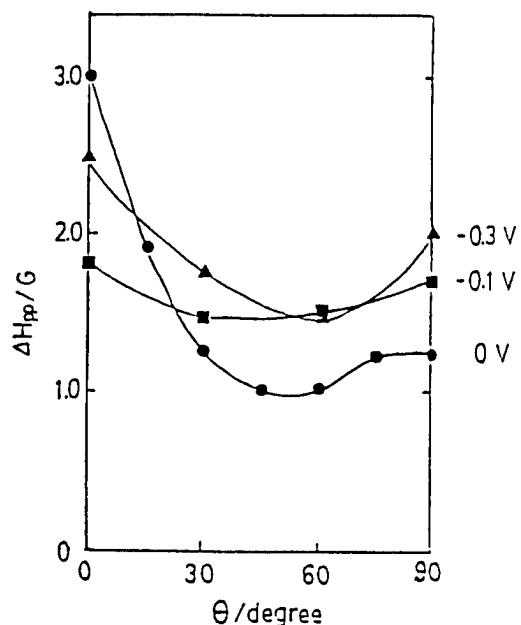


Fig. 2 Plots of  $\Delta H_{\text{pp}}/G$  vs.  $\theta$  for the ESR spectrum of the mixed LB films of  $C_{18}\text{TCNQ}$  with AME (1:1) reduced at several electrode potential.

Table 1 Conductivities of various TCNQ LB and cast films

Compound	Film	E/V vs. SCE <sup>a)</sup>	$\sigma/\text{S cm}^{-1}$ b)
$C_{18}\text{TCNQ-AME}$ (1 : 1)	LB	----c)	$< 1 \times 10^{-8}$
	LB	+0.35	$0.4 \sim 7 \times 10^{-5}$
	LB	+0.10	$1 \sim 2 \times 10^{-5}$
	LB	-0.10	$0.1 \sim 1 \times 10^{-3}$
	LB	-0.30	$1 \sim 2 \times 10^{-4}$
$C_{18}\text{TCNQ}$	cast	----c)	$< 1 \times 10^{-8}$
	cast	-0.05	$0.5 \sim 1 \times 10^{-2}$
$C_{18}\text{Py-(TCNQ)}_2$	LB	----c)	$1 \sim 2 \times 10^{-7}$
	cast	----c)	$2 \sim 5 \times 10^{-1}$
$C_{22}\text{Py-(TCNQ)}_x$ $x=1.0$	cast	----c)	$\sim 2 \times 10^{-6}$
	cast	----c)	$\sim 6 \times 10^{-6}$
	cast	----c)	$\sim 2 \times 10^{-4}$
	cast	----c)	$\sim 1 \times 10^{-2}$

a) Potential of the electrolysis in 0.1 M ethylpyridinium bromide solution.

b) Conductivities were measured in lateral direction of the film.

c) Without electrochemical treatment.

# Electrical Evaluation of Ultra-thin Organic Films on Solid Substrates

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## 1. Introduction

We established two evaluation methods of monolayer-order organic films on solid substrates, and evaluated various kinds of films; i.e., LB films of mono-alkyl lipids, dialkyl lipids, dialkylsilane, and fluorocarbon, and chemically adsorbed films of three kinds of trichlorosilane compounds. Boron-diffused Si wafers and vacuum-evaporated Cr films on glass plates were used as the substrates. The methods and results of the characterization are reported in the present paper.

## 2. Experiment

### (1) Qualitative evaluation by Cu decoration

The authors have reported that quantitative evaluation of the defects of each film is possible by the comparison of peak current value during the Cu decoration.[1] We have also reported that the defect density of dialkyl LB films was considerably decreased after thermal annealing and rinsing in an alcohol solution.[2] This time we compare the film quality of three kinds of trichlorosilane adsorbed films and dialkyl LB films on Si wafers after the treatments by Cu decoration.

### (2) Evaluation by micro-manipulating Hg probe

Vacuum-evaporated metal is widely used for fabricating MIM devices using LB films as the insulator. In that case, however, the films are intentionally exposed to high temperature and high vacuum in spite of the advantage that the films can be deposited in room temperature and at normal pressure. The film may be destroyed by the heat or the bombardment of metal atoms, and in addition, a part of the film may sublime in the high vacuum. We used the Hg probe as a top electrode which is liquid at room temperature, and used Cr as the bottom electrode which dose not amalgamate in touch with Hg. I-V characteristics at various spots on those films were measured by scanning the probe fixed on the X-Y micro-manipulating stage(Fig.1).

## 3. Results and Discussion

Electrical characterization of the films with monolayer-order thickness was found to be possible by using Hg top electrode, and clear dependence on monolayer number was found quite reproducibly (Fig.2). The dependence on the materials was also obtained as shown in Fig.3. The study on how those film materials influence the electrical properties revealed that fluorocarbon polyion complex have the highest resistivity among all of the LB films used in this experiment and the resistivity value was as high as that of bulk teflon (Fig.4).

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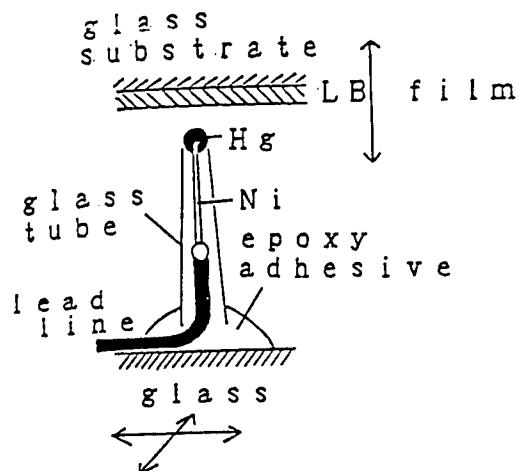


Fig.1 micro-manipulating Hg probe

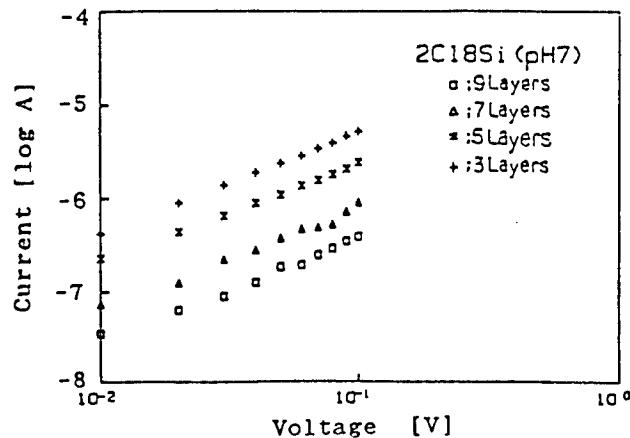


Fig.2 I-V characteristics of dialkylsilane LB films with the monolayer number as a parameter

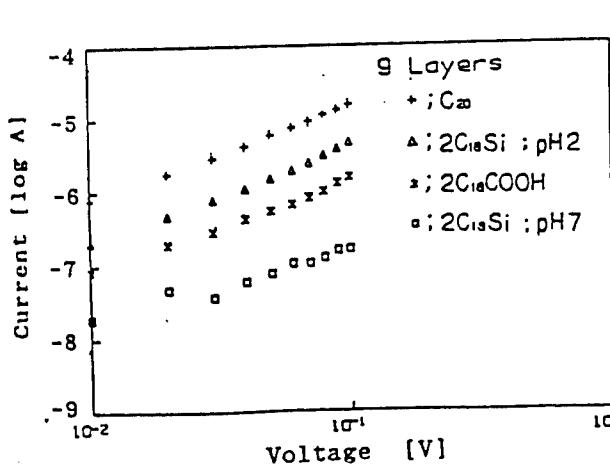


Fig.3 Dependence of I-V characteristics on the materials  
 $C_{20}$ :arachidic acid  
 $2C_{18}Si$ :dialkylsilane  
 $2C_{18}COOH$ : dialkyl carboxyl acid

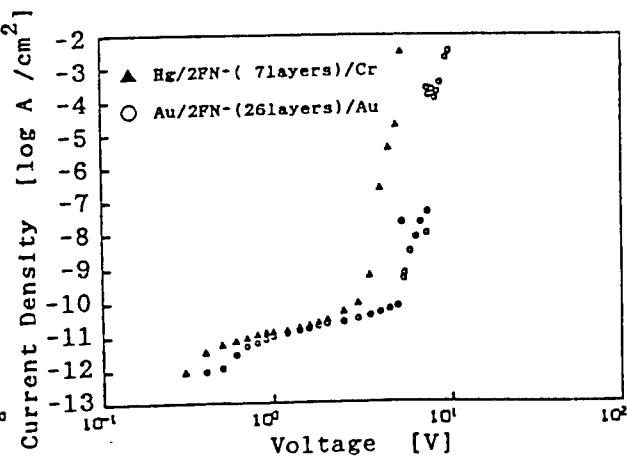


Fig.4 I-V characteristics of fluorocarbon LB Films ( $2FN^+$ ) using Hg (▲) and vacuum evaporated Au (○) as top electrodes

Photoelectric Properties of Molecular Heterojunction  
Based on Flavin-Porphyrin LB Multilayers

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Considerable interests have been directed toward the electronic and photonic functions of LB films to construct molecular electronic devices. In biological electron transport system, the rate for the electron transfer is mainly controlled by the redox potential difference between prosthetic groups such as flavin and heme.<sup>1)</sup> This suggests that the electron transfer in biomimetic molecular organizes could also be regulated by the redox potential difference. Thus, we have investigated photoinduced electron transfer in molecular organizes containing flavin and porphyrin.

7,8-dimethyl-3,10-dinonylisoalloxazine (DNI, Fig.1) was used as flavin LB molecules and hematoporphyrin(IX)bis(tridecanoyl ether)Ru(III)(P(OCH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> complex (Ru(III)HP(Ph)<sub>2</sub>, Fig.1) as porphyrin LB molecules. Flavin (or porphyrin) monolayers were deposited on an Al electrode which was vacuum evaporated onto a glass substrate. Then, porphyrin (or flavin) monolayers were deposited on the flavin (or porphyrin) monolayers. On the top of the film, three circular Al electrodes with a surface area of 0.2 cm<sup>2</sup> were evaporated<sup>2)</sup>.

Fig.2 shows transient photoresponses observed in a hetero-type sandwich cell, Al/9(RuHP(Ph)<sub>2</sub>)/10(DNI)/Al. The voltage was applied to the cell by setting the Al electrode with the RuHP(Ph)<sub>2</sub>-layer at the ground level. As shown in the figure, the responses were found unexpectedly strong at three different voltages applied: The photocurrent density with an applied voltage of 1 V peaks well above 10<sup>-6</sup> A·cm<sup>-2</sup> and steadies at a level of 5 × 10<sup>-7</sup> A·cm<sup>-2</sup>. A homo-type sandwich cell, Al/9(RuHP(Ph)<sub>2</sub>)/Al or Al/9(DNI)/Al, showed quite different photoresponses: The ratio of the photocurrent to the dark current with the homo-type cell at 1 V is less than 1.5, whereas the ratio with the hetero-type cell is about 100. It might be concluded, therefore, that the photocurrent of the hetero-type cell is mainly controlled by molecular heterojunction based on flavin-porphyrin LB multilayers. Also, it should be noted that the photoresponse spectrum is much the same in shape as the absorption spectrum of DNI monolayers (Fig.3). This result suggests that the carrier-generation mechanism in the hetero-type cell is closely related to the photoexcitation of flavin.

This work was supported by the MITI's Project of Basic Technology for Future Industries.

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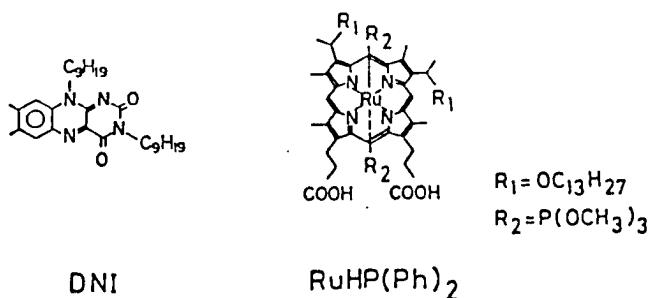


Fig.1 Structures of flavin and porphyrin molecules used for LB monolayers.

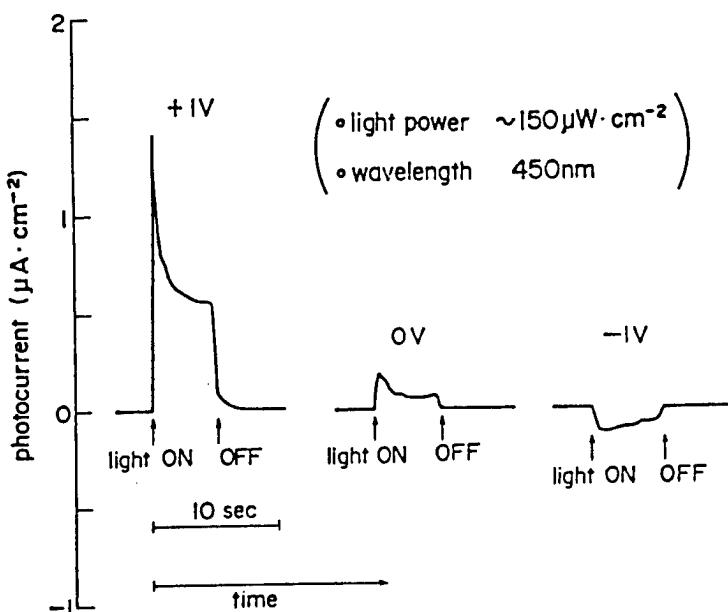


Fig.2 Transient photoresponses of Al/9(RuHP(Ph)<sub>2</sub>)/10(DNI)/Al sandwich cell.

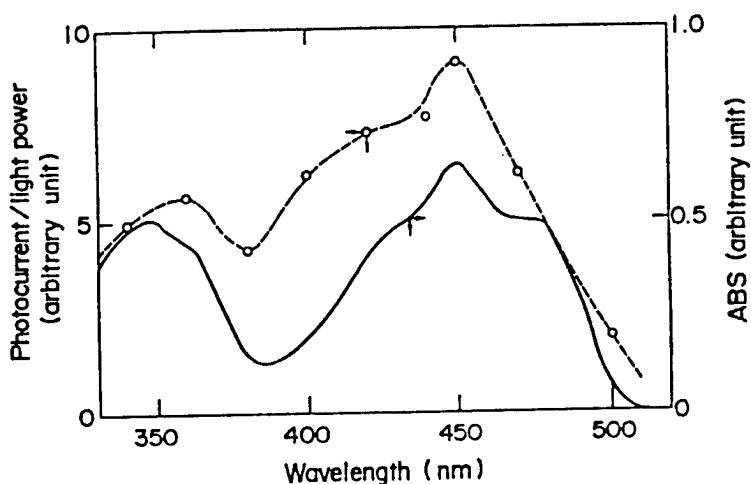


Fig.3 Photoresponse spectrum (dashed line) of Al/9(RuHP(Ph)<sub>2</sub>)/10(DNI)/Al sandwich cell and the absorption spectrum (solid line) of DNI monolayers.

## Lead Phthalocyanine LB Films

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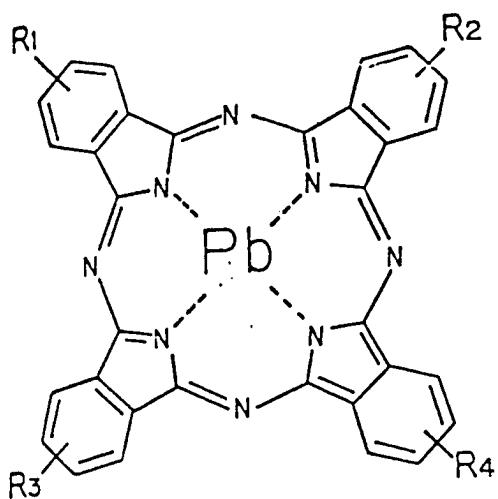
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We have studied electrical properties of vapor deposited lead phthalocyanine films and found a new switching phenomenon. This phenomenon was observed in the direction perpendicular to the c-axis of crystal different from the earlier report by Hamann in which it was explained as a field-induced order-disorder transition parallel to the c-axis. The behavior of this new type switching phenomenon was found to be varied affected by the states of the molecular assembly including the molecular orientation, the molecular stacking and its crystallinity. LB technique is very useful for investigating the relationships between the structures of the molecular assembly of lead phthalocyanine and electrical properties of them and improving the switching characteristics. By selecting appropriate substituents on the ring of lead phthalocyanine, the molecular orientation and stacking in the LB films could be controlled because of their differences in molecular interactions.

In this study, we synthesized some derivatives of lead phthalocyanine and tried to construct their LB films. Electrical properties of them were also investigated.

The structures of lead phthalocyanine derivatives employed in this study are shown in Fig.1. These structures were identified by elemental analysis, FTIR and UV-VIS spectra. Phthalocyanines are usually in aggregated form and have difficulty in constructing monomolecular layers on the water surface. The UV-VIS spectra of the solutions exhibited that substituted lead phthalocyanines in the solutions existed in non-aggregated states. So, they would be expected to form stable monomolecular layers on the water surface. Surface pressure-area isotherms of the compounds (1)-(3) are shown in Fig.2. Zero-pressure-extrapolated-areas were smaller than that of phthalocyanine ring and varied with their substituents. From the results, phthalocyanine rings were considered to be inclined at certain angles to the water surface. As the films were kept at a constant surface pressure, the film areas decreased with time (few percents decrease within initial 5 or 10 minutes). Therefore, microcrystallization might occur in these films. Current-voltage characteristics of transferred films showed different behavior from those of vapor deposited films. For example, LB films of (1) showed negative resistance. These differences were considered to result from the different molecular orientation and intermolecular interaction of LB films, in contrast to vapor deposited films.

This was performed under the management of the R & D Association for Future Electron Devices as a part of the R & D Project of Basic Technology for Future Industries, sponsored by Agency of Industrial Science and Technology, MITI.



- (1)  $R_1=R_2=R_3=R_4=-C(CH_3)_3$
- (2)  $R_1=R_2=R_3=R_4=-O-C_5H_11$
- (3)  $R_1=R_2=R_3=R_4=-O-\text{C}_6H_4-\text{CH}_2-$
- (4)  $R_1=-O-C_5H_11, R_2=R_3=R_4=H$ .
- (5)  $R_1=-O-\text{C}_6H_4-\text{CH}_2-$ ,  
 $R_2=R_3=R_4=H$

Fig.1 Molecular structure of lead phthalocyanine derivatives

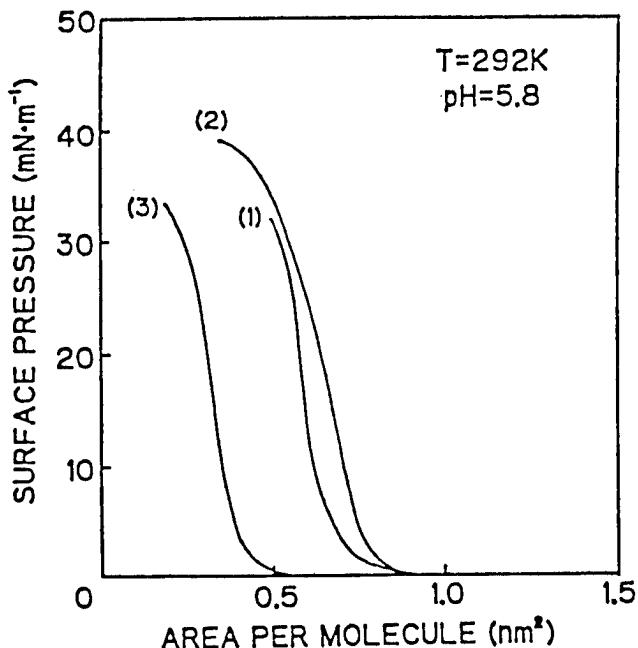


Fig.2 Surface pressure-area isotherms of (1)-(3)

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# ELECTROCHROMISM OF LUTETIUM DIPHthalocyanine LB FILMS

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Rare-earth metal diphthalocyanines show electrochromic properties; the color of their films were changed from original green to red-brown in an oxidation process, and through blue to purple in a reduction process. Most of these films have been prepared by vacuum evaporation technique, in this presentation the LB film formation of Lutetium diphthalocyanine (Pc<sub>2</sub>LuH), its electrochemical properties and electrochromic behaviors were described.

Pc<sub>2</sub>LuH was synthesized according to the kirin's method. The crude product was separated by column chromatography (silica gel, 100 mesh-up CHCl<sub>3</sub>), followed by heating at 250-260°C in a high vacuum for 1 hr. Using such purification procedures, the desired product with a satisfaction elemental analysis results was obtained.

The LB film of Pc<sub>2</sub>LuH was prepared for the first time. A stable reproducible Langmuir film was formed. From the limiting molecular area it is likely that the molecules of Pc<sub>2</sub>LuH are densely packed with a face-to-face orientation and edge-on to the water surfaces. The LB films deposited on ITO glass revealed to be a so-called Z-type up to 120 layers with the transfer ratio

maintainning at ca. 0.9.

From an X-ray diffraction pattern of 120-layes LB films of  $\text{Pc}_2\text{LuH}$ , only a diffused reflection at  $2\theta=6.3$ , corresponding the spacing length of  $14.0 \text{ \AA}$ , was observed, supposing that the molecular arrangement of this LB film is imperfect due to the lack of higher subsidiary peaks.

Comparision of the LB film and casting film of  $\text{Pc}_2\text{LuH}$ , the cyclic voltammograms demonstrate that the reversibility and electrochemical stability of LB film system is better than that of casting film system. The dependence of the peak current on the scan rate, a linearity dependence can be observed, indicating the redox reaction is diffusion-limited.

The electrochromic behaviors were investigated by in situ electronic absorption spectroscopy. The typical Q-band of  $\text{Pc}_2\text{LuH}$  was getting smaller as well as shifting to longer wavelengh in the oxidation process, on the contrary, shifting to lower wavelengh in the reduction process. These results illustrate that the redox state of  $\text{Pc}_2\text{LuH}$  is responsible for the electrochromism. Four distinguished colors, green, brown-red, blue and purple were photographed at the controlled potentials.

After about 7 hrs repetitive scanning at  $100 \text{ mV/s}$  between -0.2—0.6V, the relative Q-band intensity increased by 6%, probably as a result of the dissociation of the diphthalocyanine into monophthalocyanine.

# Low-Energy Electron Transmission Measurements on Polydiacetylene LB films

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We have investigated electron conduction through polydiacetylene LB (PDA-LB) film [1] with low-energy electron transmission (LEET) spectroscopy. LEET is a powerful technique for studying hot electron transport through a dielectric film deposited on a metal substrate. In our LEET measurement [2], monochromatic low-energy electrons were injected into a sample film in UHV (typically  $5 \times 10^{-9}$  Torr), and the transmitted current ( $I_t$ ) was measured as a function of incident electron energy ( $E_i$ ). The incident current ( $I_i$ ) was 10 pA. The current density of the incidence was so small ( $40 \sim 80 \text{ pA/cm}^2$ ) that the radiation damage of the films was found to be negligible. This is an advantage for studying organic thin films.

A monomer (heptacosa 10,12 diynoic acid) monolayer was formed on a subphase ( $10^{-3}$  M Li aqueous solution), and then UV polymerization was carried out at a constant surface pressure (30 mN/m). This film was transferred onto a Cu substrate by means of a vertical dipping method. In this way, we prepared PDA-LB films of Y-type (the number of layers  $N=1, 3, 5, 7, 9$ ). All of these films were so-called "red form".

The examples of LEET spectra at low temperature are shown in Fig.1. The band structure of the side chain mainly determines the spectral features, as in the case of n-alkane films [3] and Cd-arachidate LB films [2]. The large increase of  $I_t$ , from  $E_i=0.5 \text{ eV}$  to  $1.5 \text{ eV}$ , corresponds to the onset of the electron injection into the conduction band [3]. This means that the lower edge of

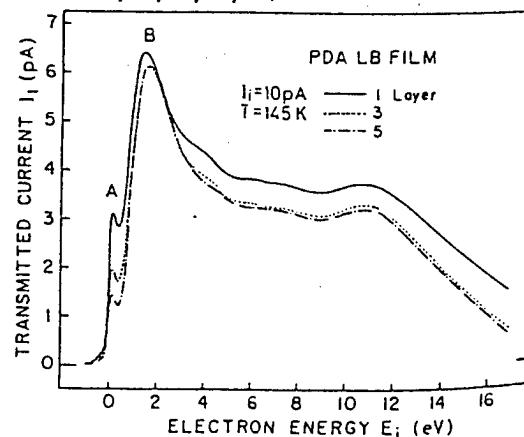


Fig.1 LEET spectra of PDA-LB films (1, 3, 5 layers). Incident current was 10 pA.

the conduction band is located at  $\approx 0.3$  eV above the vacuum level. The peaks A and B therefore reflect the electron conduction through the band gap and through the conduction band, respectively.

The intensity of peak A rapidly decreases in proportion to  $1/N$ , while peak B is nearly independent of  $N$  (Fig.2). Moreover, peak A is too large to regard as electron tunneling. According to this data, we ascribe the origin of peak A to electron diffusion or resonance tunneling via localized states in the gap.

When the film was heated, peak B became broader and shifted to the lower energy side; 0.3eV for the temperature difference of 150K (the broken line in Fig.3). This indicates that the conduction band structure of the side chain is highly affected by thermal excitation of phonons. We believe that the  $\pi$  electron bands of the main chain are modified by a temperature change, because they are sensitive to the conformation of the main chain which is strongly affected by the vibrations of the side chains.

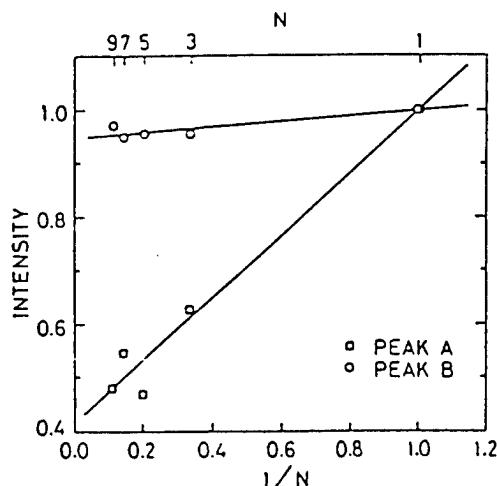


Fig.2 Intensity vs. inverse of the number of layers ( $1/N$ ). Intensity is normalized at  $N=1$ . Data was taken at 144~155K (193K for  $N=9$ ).

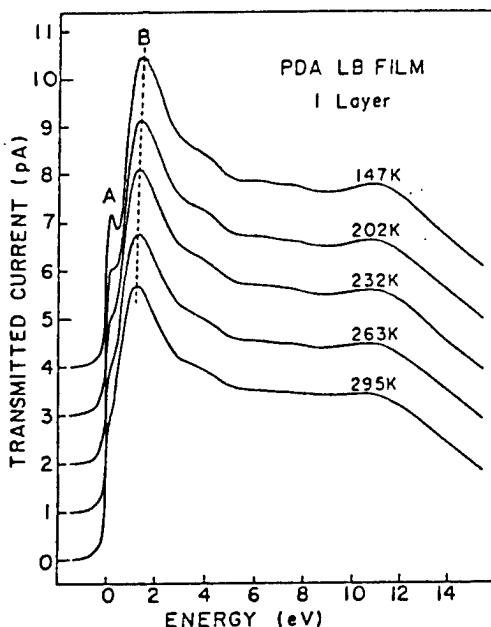


Fig.3 Temperature dependence of LEET spectra of the PDA-LB monolayer. The broken line traces the peak B.

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LB Films of Polyalkylthiophenes-Poly(isobutyl methacrylate)  
Mixed Polymers, and Their Optical and Electrical Properties

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Homogeneous LB films of poly(3-dodecylthiophene) (PDDT) and poly(3-hexylthiophene) (PHT) have been made readily by mixing them with poly(isobutyl methacrylate) (PIBM).

Poly(3-alkylthiophene) films were electrochemically prepared in nitrobenzene containing 3-alkylthiophenes and tetraethylammonium hexafluorophosphate as an electrolyte<sup>1</sup>).

Figure 1 shows the surface pressure-area isotherms for PDDT, PIBM, PDDT-PIBM mixed polymers. PDDT did not form stable monolayer by itself; the limiting area per repeating unit was too small ( $0.10 \text{ nm}^2$ ). However, when PDDT was mixed with PIBM at the molar ratios of 1:1 and 1:2, stable monolayers could be formed and had the limiting area of 0.14 and  $0.19 \text{ nm}^2$ , respectively. Molar ratio-limiting area plot of the mixed monolayers was not linear, indicating that PDDT and PIBM are miscible with each other in monolayers. The monolayers containing PHT demonstrated similar results noted above. It was possible to prepare the LB films of the 1/2 mole ratio mixed polymer successfully. The LB films were transparent and none of structures like domain and

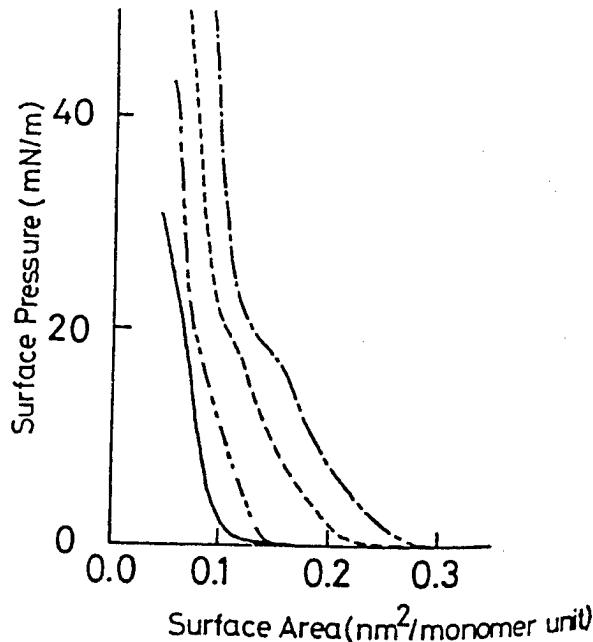


Figure 1. Surface pressure-area Isotherms for  
PDDT, PIBM, and PDDT-PIBM mixed polymers  
— :PDDT; - - - :PDDT-PIBM(1/1);  
- · - :PDDT-PIBM(1/2); - - - - :PIBM.

boundaries were observed.

The visible spectra for PDDT-PIBM mixed polymers are shown in Figure 2. The spectrum of a PDDT-PIBM solution in benzene had a peak at 2.85 eV (435 nm) corresponding to the  $\pi-\pi^*$  transition. A simple cast film, which was obtained from the PDDT-PIBM solution, showed a peak at 2.53 eV (490 nm) and a shoulder about 2.03 eV (610 nm). This shoulder is characteristic of the spectra of poly(3-alkylthiophenes) in solid states<sup>2</sup>). The LB film of PDDT-PIBM showed a peak at 2.43 eV (510 nm) and a weaker shoulder. The difference in the peak positions of the transition suggests that PDDT in the LB film has more effective conjugation than in the cast film. On the other hand, the spectrum of a cast film of PHT-PIBM had a peak at 2.41 eV (515 nm) and shoulder about 2.03 eV. The LB film of PHT-PIBM showed a peak at 2.50 eV (495 nm) without a shoulder. These results indicate that PHT in the LB film has less effective conjugation than in the cast film, as opposed to the discussion for PDDT. Moreover, the decay or the disappearance of the shoulders for the LB films would imply that poly(3-alkylthiophenes) in the films have different states of aggregation from the cast films.

The electrical and the third-order non-linear optical studies are in progress.

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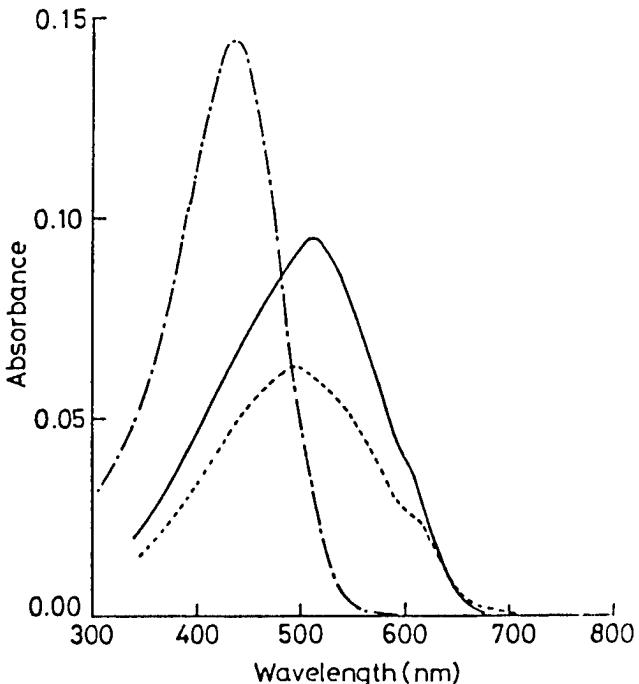


Figure 2. Absorption spectra for PDDT-PIBM mixed polymers.

— : a LB film; - - - : a cast film;  
- · - : a benzene solution.

Langmuir-Blodgett Films of Preformed Copolymers of  
N-Alkylacrylamides with Vinylcarbazole

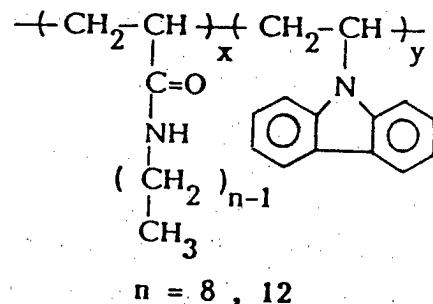
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We have been interested in Langmuir-Blodgett films of preformed polymers. It was reported that preformed poly(N-dodecylacrylamide) forms a stable condensed monolayer on the water surface and the monolayers were transferred on a solid support forming Y-type polymer LB films. In the present work, owing to add a photoactivity to the polymer LB films, the copolymers with vinylcarbazole (Scheme) were prepared and the spreading behaviors on the water surface and photochemical behaviors of carbazole chromophore in the LB film were investigated.

The copolymers were prepared with an ordinary radical polymerization of vinylcarbazole (Cz) with N-dodecylacrylamide (DDA) or N-octylacrylamide (OA). The copolymer compositions were determined by NMR spectra (DDA/Cz=7/1, 2/1, OA/Cz=4/1). A chloroform solution of the copolymers was spread on the water surface. The surface pressure( $\pi$ )-area(A) curves were shown in Fig. 1. The  $\pi$ -A isotherms with a steep rising of surface pressure and a high collapse pressure were obtained, which indicates that stable condensed polymer monolayers are formed without a help of surfactant molecule. The copolymers with DDA form more stable monolayer than that with OA. The limiting surface

Scheme



$$n = 8, 12$$

area for carbazole monomer unit was estimated to be  $0.35 \text{ nm}^2/\text{monomer}$  from the isotherms. The copolymer monolayers could be deposited onto a quartz slide in both downward and upward stroke with a transfer ratio of 1.0 (Y-type deposition). The emission spectra of the polymer LB films were measured at room temperature (Fig. 2). The spectra consist of only monomer fluorescence from carbazole chromophore and no excimer emission was obtained. The spectra were not changed with the number of layers deposited and the monomer emission intensity increased linearly with the layers. This result reveals that the carbazole chromophore is dispersed as an isolated chromophore. The homogeneous polymer LB film containing chromophore more than 30 % could be obtained by the successive deposition of the monolayer.

The photochemical behaviors of the carbazole in the polymer LB films were also investigated. The emission decay in the LB film shows a multi-exponential kinetics. The emission was quenched with stearyl viologen which is incorporated in the same layer or the adjacent layer of LB film. The quenching is due to electron transfer from the carbazole to the viologen. The detailed discussion would be carried out.

Conclusively, the chromophore can be incorporated into polymer LB film as a comonomer of poly(alkylacrylamides) which have an excellent monolayer formation properties.

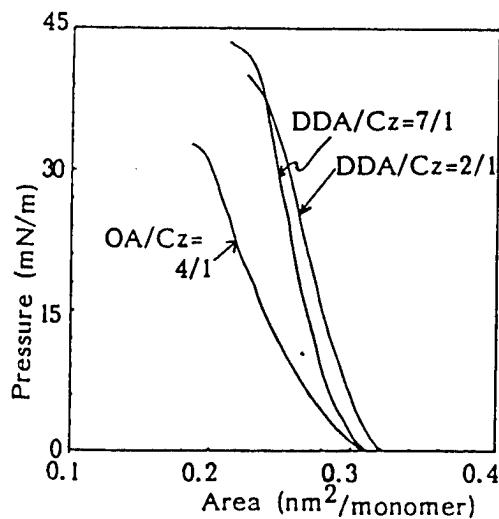


Fig. 1  $\pi$ -A isotherms for copolymers of alkylacrylamides with vinyl carbazole.

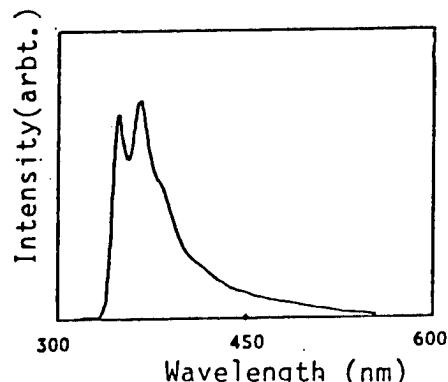


Fig. 2 Emission Spectrum of carbazole chromophore in the polymer LB film.

# Energy Transfer and Excimer Formation in Layered Polymer Films Prepared by the Langmuir-Blodgett Technique

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Photophysical properties of Langmuir-Blodgett films have been widely investigated.<sup>1)</sup> Recently, some amphiphilic polymers were found to form stable monolayers at the air-water interface and to be transferred to solid substrates. Poly(vinyl alkylals) is a type of such amphiphilic polymers, reported by Ogata et al.<sup>2)</sup> This polymer is synthesized by the reaction of poly(vinyl alcohol) with alkyl aldehydes. With the coexistence of chromophoric aldehyde, we can easily prepare photosensitive polymers with various concentrations of the chromophore and make the built-up films by the LB method. LB films prepared from preformed polymers have two remarkable characteristics.

(1) Polymer LB films are essentially amorphous and each chromophore is linked to the polymer chain with covalent bonds. Such polymers are appropriate to prevent the chromophores from forming various kinds of aggregates, and to attain uniform distribution of chromophores in the monolayer.

(2) The monolayer is stabilized both by hydrophilic groups on the main chain and hydrophobic groups as the side chain, which need not be a long alkyl chain. So, the polymer LB film usually has a thickness of ca. 1-2 nm which is fairly thinner than the conventional LB films from long-chain fatty acids. This fact means that the

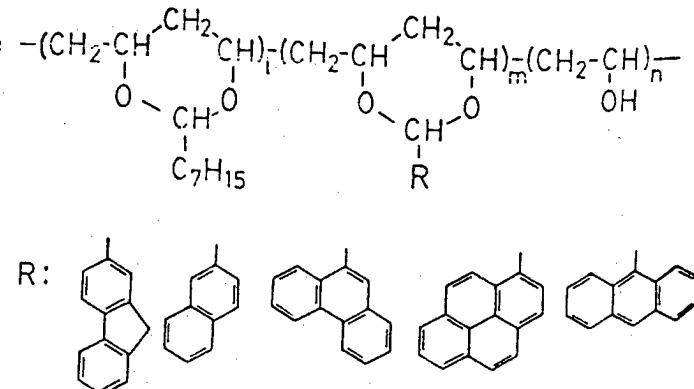


Figure 1

incorporated chromophores easily carry out interesting photo-physical interactions, e.g., energy transfer between neighboring layers.

In this paper, these characteristics will be demonstrated by using poly(vinyl octals) with various kinds of chromophores, fluorene, naphthalene, phenanthrene, pyrene, and anthracene, as shown in Fig. 1.

Excimer formation in the films with pendant pyrene groups was utilized as a molecular probe for the aggregation of chromophores. The results are compared with the data obtained for the monolayer films consisting of stearic acid. Fluorescence spectra show a small concentration of excimer forming site and uniform distribution of pyrene in the LB film. Furthermore, the time-resolved measurements with picosecond laser system indicate the migration of excitation energy among pyrene chromophores.

Energy transfer between chromophores spaced by multi-layered films was carried out by some pairs of energy donor (D) and acceptor (A) polymers. As expected from the layered structure, the transfer process is controlled by the sequence and the spacing of polymer films. The stepwise energy transfer from D to A<sub>1</sub> and A<sub>2</sub> layers is also examined by the measurement of time-resolved fluorescence spectra.

In this system, it will be shown that the polymer LB film is a promising material to realize an artificial molecular assembly in which designed photophysical and photochemical processes can be achieved.

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Photoinduced Intramolecular Electron Transfer across Monolayers  
Consisting of Linear A-S-D Triad Amphiphilic Molecules

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Previously, we reported photoelectric conversion by monomolecular layer assemblies which consisted of triad molecules and fatty acids.<sup>1)</sup> The triad molecule had three functional moieties within a molecule, i.e. an electron acceptor (A), a sensitizer (S), and an electron donor (D) moiety. These moieties were linked covalently one another by normal hydrocarbon chaines in the form of S-A-D, where "-" represents a hydrocarbon linkage and the A-D linkage was longer than the S-A linkage. In addition, hydrophobicity was required for the S and D moieties, whereas the A moiety had to be hydrophilic for preferable orientation of three functional moieties across the monolayer in the order of A, S, and D. This spatial arrangement is indispensable for efficient charge separation via multistep electron transfer as in the primary process in the reaction center of photosynthesis.<sup>2)</sup> It was found, however, that this spatial arrangement was only attained only under the high surface pressures.

In this report, we studied photochemical properties of a newly synthesized linear type A-S-D triad molecule in which three moieties are linked by hydrocarbon chains in the order of A, S, and D. The linear type triad molecule enables to make the orientation of A-S-D in a monolayer more readily compared with the previous bending type of triad molecules, S-A-D. Both types of triad molecules consist of viologen, pyrene, and ferrocene units as the A, S, and D moieties, respectively.

The linear type A-S-D triad molecule and the reference compound without the D moiety, i.e. A-S- bifunctional molecule, were synthesized by the Friedel-Crafts acylation followed by the reduction of the resulting carbonyl group. Each hydrocarbon linkage of A-S-D and A-S- contains six carbons as shown in Fig. 1. These compounds were characterized by NMR, UV spectroscopy, and elemental analysis. The LB films of A-S-D and A-S- were

studied by UV and fluorescence spectroscopy. The Au-OTES coated with monolayers of these molecules were prepared by the LB method and the photocurrents were measured on them.

The absorption spectrum of an A-S-D ethanol solution was the same as superposition of the individual absorption spectra of the A, S, and D units, which indicates that the A, S, and D moieties do not interact with one another in the ground state. The dramatic decrease in the fluorescence intensities of both compounds indicates that the fluorescence of the S moiety was quenched effectively by the A and/or D moieties. The photocurrents across the monolayer of these molecules were observed in the direction from A to D for A-S-D and from A to S for A-S-. which indicates that the photoinduced intramolecular electron transfer occurs from D to A and S to A, respectively. The rapid responding photocurrent for A-S-D was larger than that for A-S-. This result indicateds that the D moiety of A-S-D contributes to the efficient photoelectric conversion, as we would expect.

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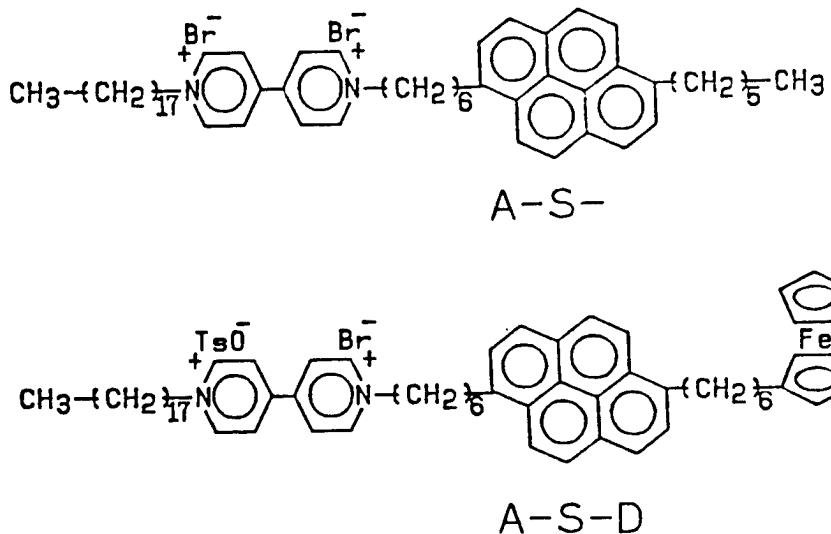


Fig. 1 Structural formulae of A-S- and A-S-D molecules.

# Photochromism of Amphiphilic Azobenzene Derivatives in their LB Films Prepared as Polyion Complexes with Ionic Polymers

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The LB films of photochromic material are of interest as possible high density information storage media and light switching devices. cis-trans Photoisomerization of long-chain azobenzene derivatives was inhibited in their pure LB films.<sup>1)</sup> Recently, however, Yabe et al. have reported that azobenzene guest molecules in the host-guest LB films showed photochromic behavior with complete reversibility owing to the free volume of the cyclodextrin cavity.<sup>2)</sup> On the other hand, Kunitake et al. have already reported that monolayers of azobenzene ammonium amphiphiles are stabilized by formation of insoluble polyion complexes with potassium poly(vinylsulfate).<sup>3)</sup> In addition, we have found that the cross sectional area of the amphiphilic molecule is determined by the size of water-soluble polymer counter ions used.<sup>4)</sup>

In this paper, we will report the detailed study of the cis-trans photoisomerization of azobenzene amphiphilic derivatives in their LB films. These LB films were formed as polyion complexes of the azobenzene amphiphiles with several kinds of cationic polymers which have amines, alkyl ammoniums, or alkylpyridiniums as their side chains.

The azobenzene amphiphilic derivatives and the water-soluble polymers used are shown in Fig. 1. The cross sectional areas of 8A5 at 30 mN m<sup>-1</sup> and those extrapolated to 0 mN m<sup>-1</sup> obtained from  $\pi$  - A isotherms are listed in Table 1 for six kinds of counter ions. These results clearly indicate that we could control the cross sectional area of the ionic functional amphiphile by choosing the size of the polymer counter ions.

The UV-visible absorption spectra of the 8A5-PVB polyion complexed LB films on the quartz plate are shown in Fig. 2. The spectrum (a) for the film as deposited corresponds to the trans isomer of 8A5 and the spectrum (b) obtained by UV irradiation shows partial conversion from trans isomer to cis isomer of 8A5 in the LB films. The spectrum (c) obtained by visible light irradiation shows that the trans isomer was recovered. A slight difference in between spectra (a) and (c) was observed in the first cycle. However, in the next five cycles with alternative irradiations, the change in absorbance was almost reproducible.

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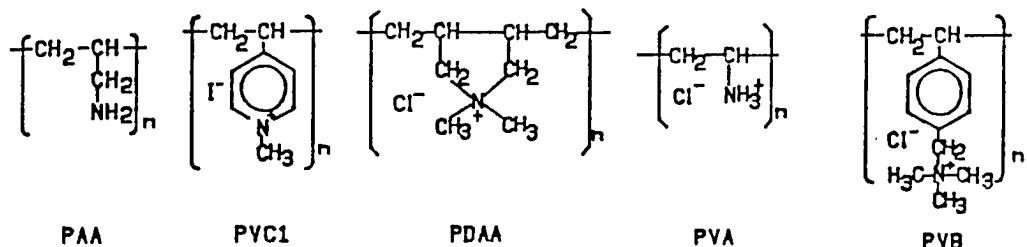
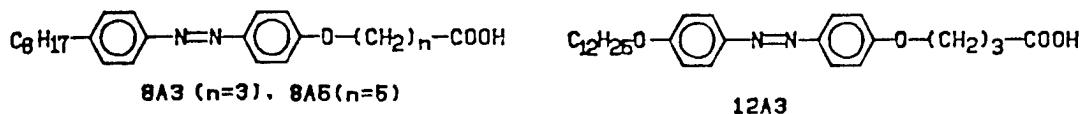


Fig. 1. Structural formulae of the azobenzene amphiphilic derivatives and the water-soluble polymers.

	area per 8A5 molecule/nm <sup>2</sup>	
	at 30 mN m <sup>-1</sup>	extrapolated to 0 mN m <sup>-1</sup>
$\text{Ba}^{2+}$	0.25	0.32
PVC1	0.41	0.61
PAA	0.39	0.50
PVA	0.37	0.54
PVB	0.42	0.63
PDAA	0.45	0.76

Table 1. The dependence of the cross sectional area of 8A5 on kinds of counter ions.

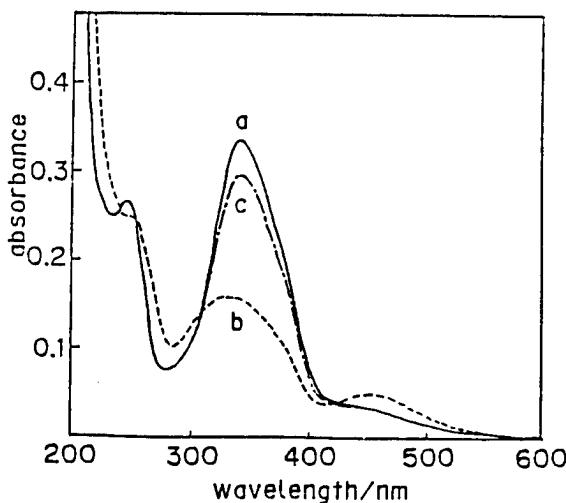


Fig. 2. Change in UV-visible absorption spectra of the 8A5-PVB LB multilayer deposited on the quartz plate upon irradiation. (a); a virgin film as deposited, (b); after UV light (365 nm) irradiation for 60 min, (c); after visible light (435 nm) irradiation for 60 min.

# Novel Molecular Optical Memory of Luminescent LB Films

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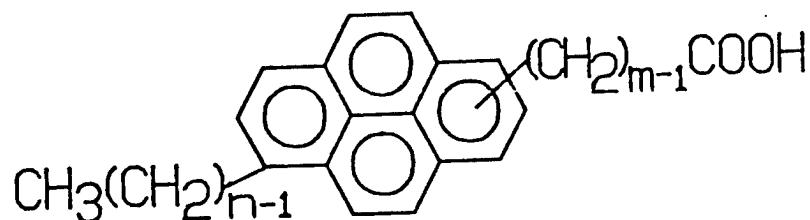
The LB films of photochromic material have been studied recently as possible high density information storage media. In this laboratory, however, the more sensitive information storage LB films have been developed by utilizing rapid quenching of the fluorescent LB films of pyrene derivatives by the photo-oxidative products. In the previous study, 10-(1-pyrene)decanoic acid (PDA) was used as the amphiphilic pyrene derivative, although it was found that a pure monolayer of PDA on water was unstable and mixing with arachidic acid was needed to stabilize the monolayer. Furthermore, the fluorescence microscopic study revealed segregation of the pyrene-tailed fatty acid phase from the arachidic acid phase and therefore inhomogeneous pyrene density in the mixed film plane, which is unfavorable for high density information storage.

In this paper, we will report improved monolayer properties of newly synthesized pyrene amphiphilic derivatives, in which the pyrene moiety is located not at the end but in the middle of the alkyl chains of fatty acids. These new compounds are 6-(1-(6(8)-decyl)pyrene)-hexanoic acid (DPHA) and 10-(1-(6(8)-hexyl)pyrene)decanoic acid (HPDA) and their structural formulae are shown in Fig. 1.

The fluorescence spectra of the monolayers of DPHA, HPDA, and their equimolar mixture deposited on quartz are shown in Fig. 2. All spectra show a monomer emission and an excimer emission band at ca. 400 and 450 nm, respectively. Relatively strong monomer emission observed for the mixed monolayer is ascribable to the zigzag arrangement of pyrene moieties in the monolayer illustrated in the inset.

Photochemical oxidation of the mixed LB films in the presence of molecular oxygen was also studied. The much higher rate in the decrease in the fluorescence intensity than that in the UV-visible absorbance due to pyrene moieties can be ascribable to the energy transfer quenching of the photoexcited pyrene moieties by the photo-oxidative products. The energy transfer quenching of the Forster type was confirmed by examining dependence of the fluorescence quenching on the spacer thickness between the monolayers of the pyrene moieties and the photo-products in the LB films, which were prepared in the following procedure: a mixed monolayer of DPHA and HPDA was first UV irradiated for 160 min, then covered with another fresh mixed monolayer with intervention of an appropriate number of spacer layers of arachidic acid. The lateral quenching in the UV irradiated

monolayer was also simulated by the mixed monolayer consisting of DPHA, HPDA, and a synthesized model compound for one of the photo-oxidative products. Application of the amplified decrease in the excimer emission in terms of the quenching by photo-products to a very sensitive photo-responsive memory was also suggested.



D P H A (n=10, m=6 )

H P D A (n= 6 ,m=10)

Fig. 1. Structural formulae of newly synthesized pyrene amphiphilic derivatives, DPHA and HPDA.

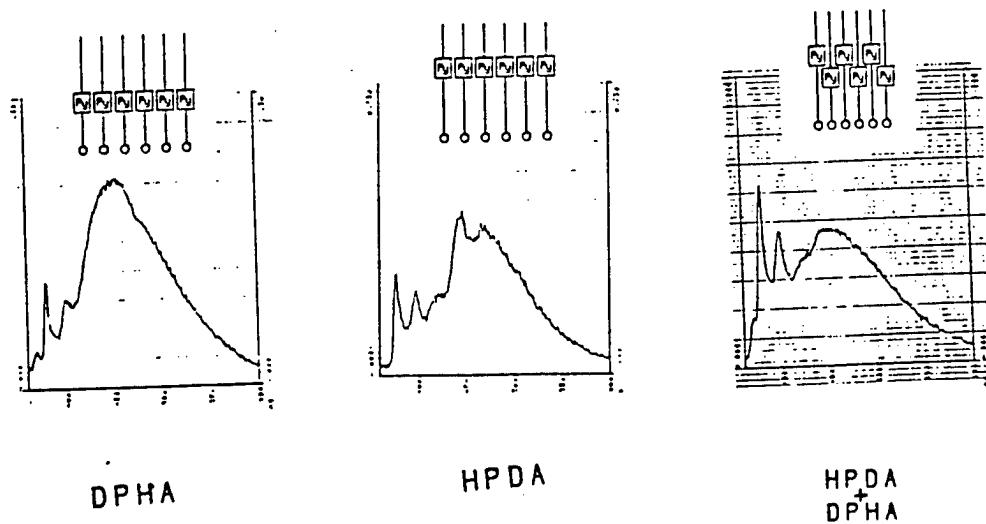


Fig. 2. Fluorescence spectra of DPHA, HPDA, and mixed monolayers together with the corresponding schematic representations of the supposed structures of the monolayers.

# LIGHT-INDUCED MOLECULAR ORIENTATION IN LB FILMS OF SPIROPYRAN

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It was found that the molecular orientation of photochromic J-aggregates in an LB film could be contorolled by the successive irradiation of linearly polarized visible laser and unpolarized UV light. A spirobopyran molecule in an LB film changes to a photomerocyanine molecule by the irradiation of UV light and then forms the J-aggregates at about 30 - 40 °C .The J-aggregate disaggregates and returns to spirobopyran form again by heating above 50°C[1]. It was obtained that this disaggregation occurred also by the irradiation of HeNe laser. Using linearly polarized HeNe laser ,the linear dichroism was revealed in J-band (absorption band for J-aggregates ). Furthermore, these disaggregated spirobopyran molecules changed to photomerocyanine form and spontaneously re-formed the J-aggregates by the irradiation of UV light . In this re-formation, the degree of linear dichroism becomes higher.

The sample films were prepared by Lamgmuir-Blodgett method. The mixed solution of spirobopyran(SP1822 chemical structure is shown in Fig.1) and arachidic acid (AA) applied on to an aqueous subphase containing about  $4 \times 10^{-4}$  M CdCl<sub>2</sub>, to form a monolayer under surface pressure of 20mN/m. The molar ratio of the mixture solution was SP:AA=1:2.The pH value and temperature of subphase were 6.8 and 20°C,respectively. 20 monolayers deposited on a glass substrate.

For the aggregation and the disaggregation of J-aggregates, UV light(about 350nm) and linearly polarized HeNe laser were used, respectively. The change in polarized absorption spectra were measured at 40°C under the irradiation.

The LB film of J-aggregates for this investigation was prepared from the LB film of spirobopyran by 20 minutes irradiation of UV light at 40 °C. The polarized absorption spectra of this film are shown in Fig.2 a<sub>1</sub>,a<sub>2</sub>. The molecular orientation was isotropic in the film plane, because the orientaion of the J-aggregate domain was having randam distribution . Fig.2 b<sub>1</sub>,b<sub>2</sub> show the polarized absorption spectra after 3 minutes irradiation of linearly polarized HeNe laser. Spectra b<sub>1</sub>,b<sub>2</sub>were parallel and perpendicular to the polarization direction of the laser, respectively. Due to the disaggregation of J-aggregates, absorption of J-band decreased sharply. Then, after 16 minutes irradiation of unpolarized UV light, the perpendicular absorption remarkably increased and exceeded a<sub>1</sub>, while parallel absorption showed a slightly increase as shown Fig.2 c<sub>1</sub>,c<sub>2</sub>.

Before any irradiation, distribution of J-aggregates orientation was at randam. By the irradiation of linearly

polarized HeNe laser, the linear dichroism was revealed because the J-aggregate whose transition dipole was more parallel to the polarization direction of the laser disaggregated more rapidly. By the successive irradiation of unpolarized UV light, disaggregated spiropyran molecules returned to photomerocyanine form again and were deposited to the remained J-aggregates and made better molecular orientation.

This light-induced molecular orientation method will enable to design the in-plane molecular orientation in LB films.

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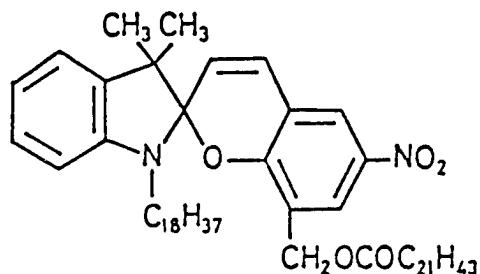


Fig.1 Chemical structure of spiropyran SP1822.

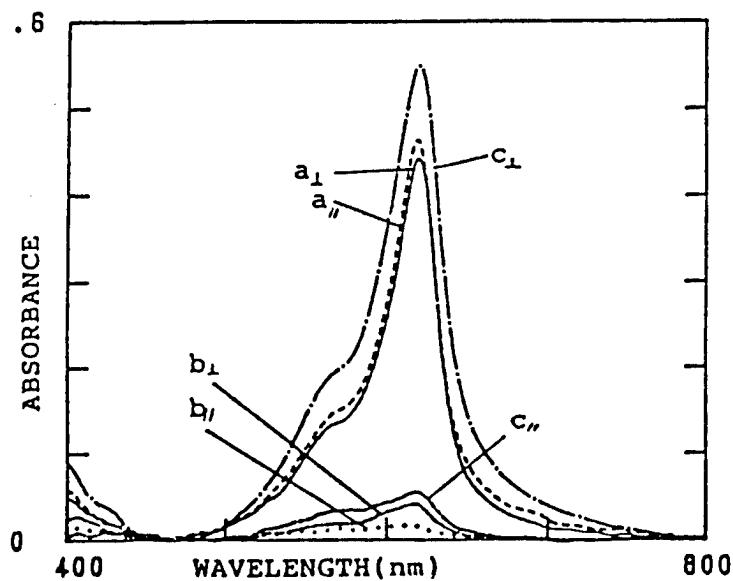


Fig.2 Polarized absorption spectra of SP1822. Spectra  $a_{\parallel}$ ,  $a_{\perp}$  denote parallel and perpendicular to the polarization direction of HeNe laser, respectively.  $a$  : after 20 min. irradiation of unpolarized UV light at 40 °C on as-deposited LB film of spiropyran.  $a \rightarrow b$  : 3 min. irradiation of linearly polarized HeNe laer.  $b \rightarrow c$  : 16 min. irradiation of unpolarized UV light.

OPTICAL AND ELECTRICAL PROPERTIES OF SELECTIVELY ADSORBED  
LANGMUIR-BLODGETT FILMS BASED ON THE INTERACTION BETWEEN TWO DYES

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By the use of the adsorption Langmuir-Blodgett technique, the LB films containing water-soluble functional dyes can be fabricated[1]-[4]. We applied this method to fabricate two-dyes systems (one has a long alkyl chain and another has no long alkyl chain, which is water-soluble), and investigated the optical and electrical properties of the films and the interaction between two functional dye molecules by X-ray diffraction, absorption spectrum and photo-electric measurements.

Figure 1 shows the materials employed in our study. We used two kinds of spreading materials as follows:

(1) AR(arachidic acid)

(2) Mixture of AR and MC(merocyanine-dye with long alkyl chain, showing the properties of p-type semiconductor[5][6]); the molar mixture ratio of AR and MC is 2:1.

Monolayers of these materials were spread on the aqueous subphase containing  $4 \times 10^{-4}$  M CdCl<sub>2</sub> and  $3 \times 10^{-5}$  M MG(malachite-green without long alkyl chain, which is a water-soluble cationic dye and shows the properties of n-type semiconductor[5][6]). The monolayers consisting of these materials were successfully transferred on a glass substrate by the conventional Langmuir-Blodgett technique.

Figure 2 shows the absorption spectra of 15 layers samples, each curve corresponding to (1) and (2) in figure 1. Both the curves show the peak at 650 nm originated from MG molecules. These results indicate that MG molecules in the water were adsorbed to spreading molecules(AR or MC) on the water. By comparing the intensity of the peak at 650 nm, it is shown that the quantity of MG adsorbed to MC is about 4 times larger than that of MG to AR and MG molecules are selectively adsorbed to MC molecules.

Figure 3 shows the photocurrent-light intensity characteristics of the sample(2) sandwiched between Al and Au electrodes. In this experiment, the sample was illuminated by two lights (each wavelength corresponds to MC(540 nm) and MG(632.8 nm) absorption peak wavelength) and the intensity of 540 nm light was fixed. Negative properties were observed in these curves, and this phenomenon seems to be concerned with the interaction between trap-centers of MC and MG.

From these properties and a structural characterization, we conclude that two functional dyes are packed face to face each other in the LB-films and the special interaction exists between p- and n-type functional dyes.

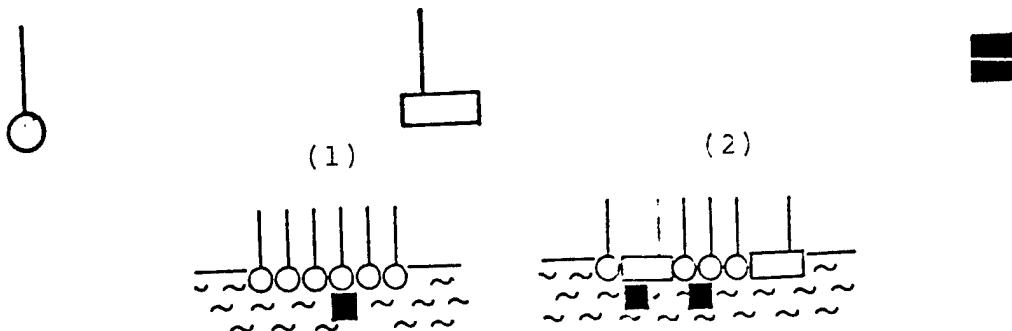
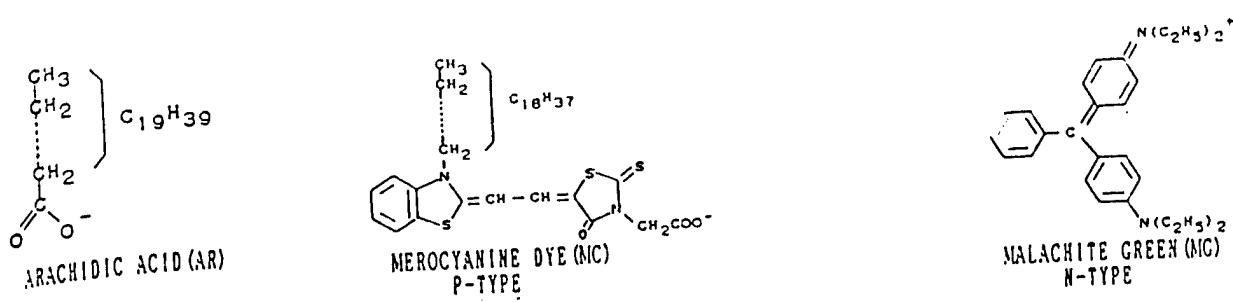


Fig.1 Chemical structures of the materials used in this report.

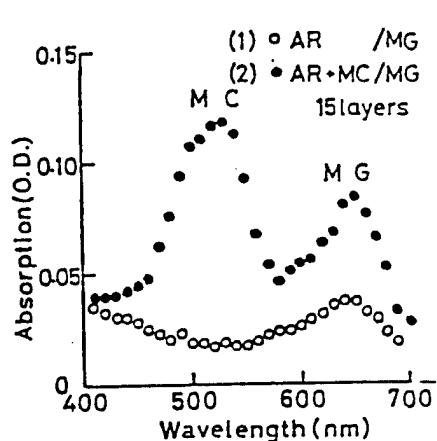


Fig.2. Absorption spectra of LB films.

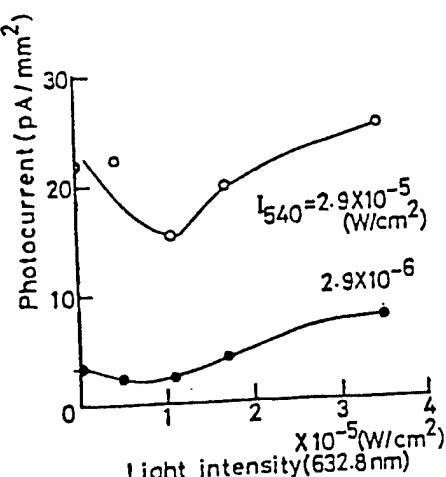


Fig.3. Photoelectric properties of Au(MC+AR/MG)Al sample.  
Light intensity of 540nm ( $I_{540}$ ) was fixed.

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# Interaction of Silver Particle with Adsorbed LB Films

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The experimental findings reported herein show that LB films can be used as a tool of the mechanical investigation of the enhanced absorption of the adsorbed dyes on silver island films. The enhanced adsorption is one of the surface enhanced processes such as the surface enhanced Raman scattering (SERS) and the enhanced fluorescence. There still exists a controversy of the mechanism of the surface enhanced processes whether it is electromagnetic or chemical. Recently LB films have been used as the tools of the mechanical investigation of the SERS (1), the enhanced fluorescence (2). The enhanced absorption also has been attracting the interest of several scientists (3). However, LB films have not been used to investigate the mechanism of the enhanced absorption so far. In this report, we employed LB films as a tool of the mechanical study of the enhanced absorption of the adsorbed dyes on silver island films and made it sure that the mechanism is electromagnetic in nature.

Silver island films were prepared by vacuum evaporation on glass substrates. The thickness of the silver island film was ca. 5 nm. N,N'-dioctadecyl Rhodamine B (RhB derivative) was deposited on glass substrates or silver island films by the conventional LB method. The thickness of one monolayer of the RhB derivative was ca. 2 nm.

Figure 1 shows the absorption spectra of LB films of the RhB derivative on the glass substrates. As the number of the monolayer increased, the absorbance increased monotonously. The peaks of absorbance are at 550 nm. Figure 2 shows the absorption spectra of the LB films of the RhB derivative on silver island films. When no LB film was deposited (A), the plasmon excitation band of silver particles was observed with the peak at 450 nm. When two layers of the RhB derivative were deposited (B), the absorbance ranging 420 nm to 750 nm was enhanced, and the new peak at 565 nm appeared. When four and six layers were deposited (C,D), the absorbance was also enhanced. However, the difference in the absorbance between (C) and (B) became smaller.

than that between (B) and (A), and the difference in the absorbance between (D) and (C) also became smaller than that between (C) and (B). The new peak slightly red-shifted. These observations indicate that enhancement factor of enhanced absorption became smaller. When eight layers were deposited, the spectrum (E) of Figure 2 was almost superimposition of the spectrum (D) of Figure 2 and the spectrum (A) of Figure 1. This indicates that the enhanced absorption does not occur for the eighth layer of the RhB derivative.

The experimental observations described above strongly imply that the mechanism of enhancement absorption is electromagnetic and not chemical. The interaction of silver particles with the adsorbed LB films gradually decreases as the distance between the silver particles and the adsorbed LB films increases. And when the distance between the silver particles and the dye molecules became longer than ca. 10 nm, the enhancement factor became almost unity. These facts indicate that the enhanced adsorption satisfies the distance dependence as electromagnetic force.

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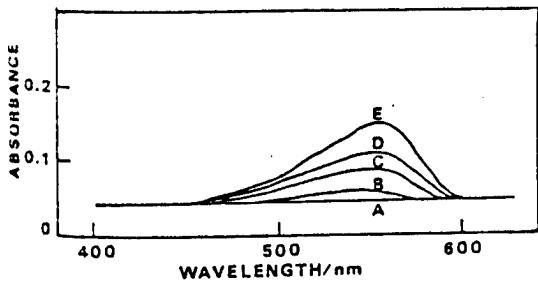


Fig.1 Absorption spectra of RhB derivative LB films on glass substrates. (A) 0 (B) 2 (C) 4 (D) 6 (E) 8 layers

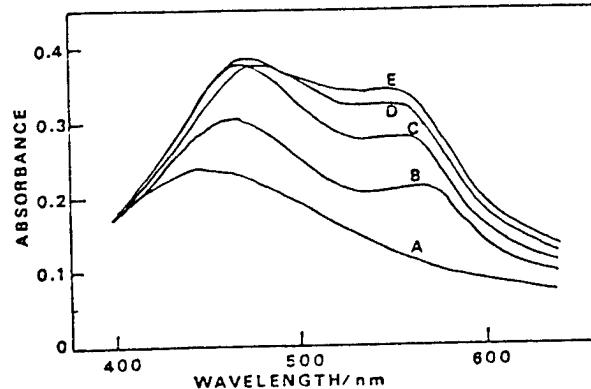


Fig.2 Absorption spectra of RhB derivative LB films on silver island films. (A) 0 (B) 2 (C) 4 (D) 6 (E) 8 layers

# Preparation and Characterization of Protein LB Films

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A variety of studies on biochemical functions of multilayer protein films have been conducted during the past two decades.

Recently these multilayer films have been considered as possible elements of new biosensors and bioelectronic devices of the near future. The Langmuir-Blodgett technique is one possible and available method for the preparation of monolayer and multilayer lipid films. Several papers concerning the changes in protein conformation at the interface between air and liquid surface have been published. Stabilization of protein at the interface, however is strongly needed for further investigations.

We describe here the preparation of a protein monolayer of bovine serum albumin( BSA) which can be developed at the air-water interface, and stabilization of the BSA monolayer using a cross-linking agent. As a result of cross-linking, the BSA monolayer was fixed and stabilized. The cross-linked-BSA film was used as a base protein film, and other functional proteins such as antibody and binding proteins were deposited on top of this BSA base film. Antibody and binding proteins were immunochemically reacted with the BSA film. Protein films consisting of protein other than BSA could be deposited on the BSA base film.

BSA was dissolved in distilled water to a final concentration of 0.5mg/ml. The BSA solution was spread over the aqueous

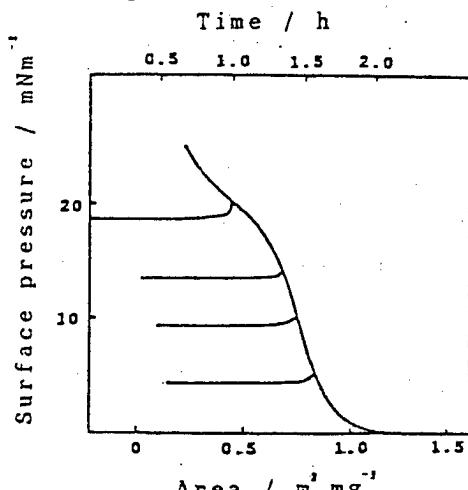


Fig.1 Surface pressure-area and Surface pressure-time curves of BSA at air-water interface

Fig.2 Surface pressure-time curves of BSA at air-water interface

— with GA

--- without GA

surface. The monolayer film was prepared at a surface tension of 14mN/m. GA-treatment was performed at this retained tension by the addition of 15ml of 50%GA into the subphase trough. The resulting GA treated and nontreated protein layers were transferred to an alkylsilanated hydrophobic glass surface.

Figure 1 shows the surface pressure-area(F-A)curve and surface pressure-time(F-T)curves,for the formed BSA monolayer. The F-A curve had an inflection point in the pressure range from 13mN/m to 15mN/m. The F-T curve shows that the surface pressure decreased abruptly when the surface area was fixed, following which a gradual decrease in the surface pressure was observed. Figure 2 represents the F-T curve of BSA molecules which were crosslinked with glutaraldehyde. Decrease in surface pressure was not observed. BSA molecules at the interface became insoluble after the aldehyde modification. Anti-BSA antibody was immunochemically reacted with the BSA film.

Protein A- $\beta$ -galactosidase(pro A- $\beta$ -gal)conjugate was then bound to the antibody which was deposited on the BSA film. Figure 3 shows the enzyme activity of  $\beta$ -gal,measured spectrophotometrically using  $\alpha$ -nitrophenyl- $\beta$ -galactopyranoside(ONPG) as substrate. At deposition concentrations exceeding  $10^{-3}$  mg/ml,an increase in anti-BSA antibody binding to the BSA base film was observed as measured by an increase in  $\beta$ -gal enzyme activity. This increase continued until saturation occurred above  $10^{-1}$  mg/ml. These results suggest that the BSA-thin film can be employed as a base protein membrane for deposition of a functional thin layer in the construction of solid-phase matrices such as immuno-membranes(Fig.4).

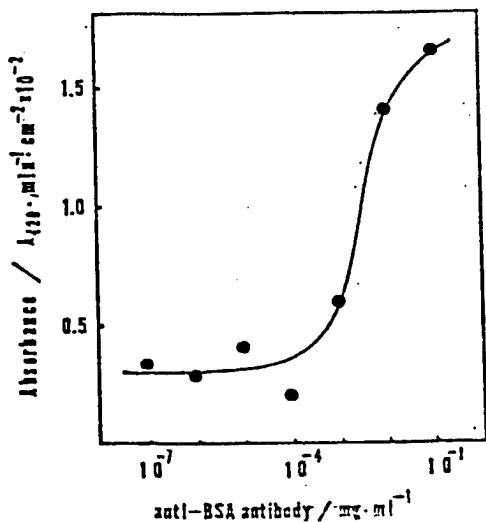


Fig.3 Immunocomplexation at different antibody concentrations

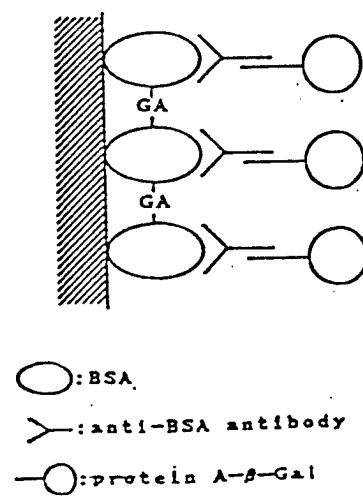


Fig.4 Schematic illustration of protein layers

# Langmuir-Blodgett Films of an Enzyme-Lipid Complex for Glucose Sensor Membranes

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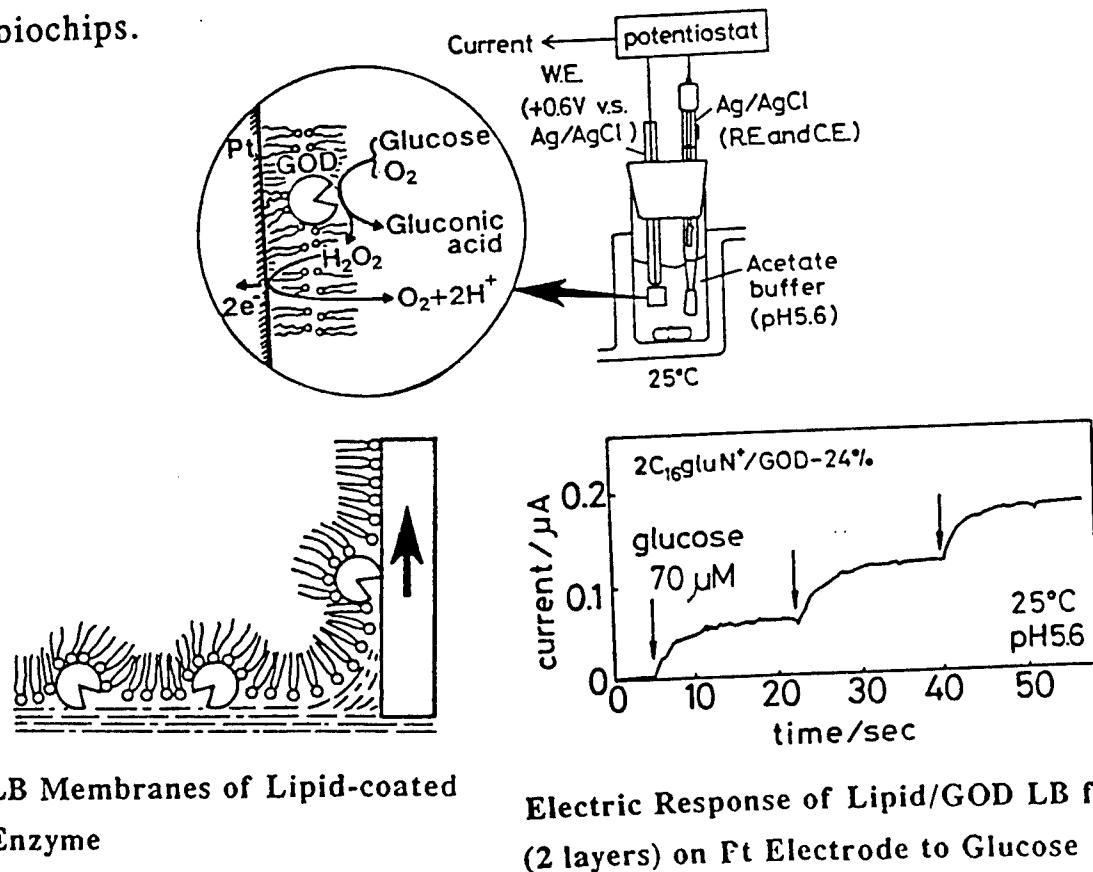
Recently, we observed that lipid-coated enzymes could be prepared by mixing aqueous solutions of enzyme and synthetic lipids without causing denaturation and the obtained enzyme-lipid complex became soluble only in organic media. For example, lipase-lipid complex has been found to function as a catalyst for esterification in a high enantioselective manner in homogeneous and nonaqueous organic solvents.<sup>1,2)</sup>

In this paper, we show that a glucose oxidase (GOD)-lipid complex can form a stable monolayer on a subphase and the Langmuir-Blodgett (LB) films deposited on a Pt electrode act as a glucose sensor membrane.<sup>3)</sup>

Buffer solutions of GOD and aqueous dispersion of dialkyl amphiphiles were mixed and precipitates were freeze-dried. A benzene solution of the obtained GOD-lipid complex was spread on pure water at 20 °C. A platinum electrode was lowered and risen through the monolayer of the GOD-lipid complex at the surface pressure of 40 mN m<sup>-1</sup> (Y type 2 layers, transfer ratio 1.0 ± 0.1). The Pt electrode coated with the GOD-lipid complex was set in acetate buffer (pH 5.6) and +0.6 V potential was applied against Ag/AgCl counter electrode. When glucose solution was injected, amperometric response was observed within 5 s and a good linear

correlation between currents and glucose concentrations was observed.

The complex formation by covering the surface of enzymes with synthetic lipids is a useful technique to get a stable monolayer and LB films of enzymes without causing denaturation. The enzyme-lipid complex will become a new tool to built-up water-soluble proteins on a biological electric components, so called the biochips.




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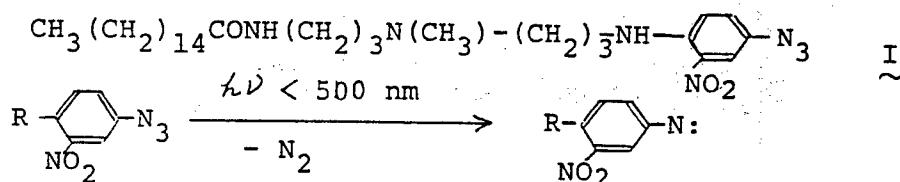
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Monolayers of a Photoreactive Phenylazide Amphiphile  
for Immobilization of Bioactive Proteins

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Use of monolayer assemblies as media to accommodate bioactive proteins serves as a promising means to provide biofunctional membranes. Biosensors have been studied employing monolayers of fatty acids, esters, or amines in which enzyme molecules are incorporated via adsorption through hydrophobic and/or coulombic interactions.<sup>1)</sup>

We report here a new type amphiphilic compound I, which is capable to immobilize protein molecules not only by its high adsorptivity to proteins but also by photochemical linking reaction involving the highly reactive phenyl nitrene.<sup>2)</sup>



I was synthesized by treating 4-fluoro-3-nitroaniline with sodium nitrite to diazotize and with sodium azide to produce an azide derivative, the latter being reacted with N,N-bis(3-aminopropyl) methylamine and then with palmitoyl chloride and triethylamine. The crude product was purified by silica-gel chromatography using CHCl<sub>3</sub>/MeOH(20/1) as eluent.

$\pi$ -A isotherm of the monolayer of I spread from CH<sub>2</sub>Cl<sub>2</sub> solution on a neutral subphase at 20°C is given in Fig. 1. Two-dimensional orientation in the monolayer was investigated by reflection-absorption FT-IR spectroscopy (RAS) for monolayers formed on a gold substrate. Comparison of the RAS result with a spectrum of a bulk sample showed that the azide group as well as the alkyl chain are both oriented perpendicularly to the film plain.

Glucose oxidase (GOD, from Boehringer Mannheim) was used as an enzyme to be immobilized. Strong adsorption of GOD to I was revealed by observation of rapid

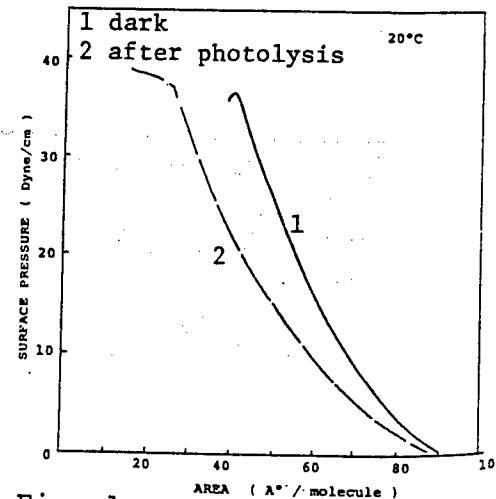


Fig. 1

increases in surface pressure for monolayers formed on dilute solutions of GOD (Fig. 2). Adsorption was also achieved by dipping the LB film of I formed on a substrate into a dilute solution of GOD. In a typical experiment, one monolayer was deposited on an alkylsilane-treated glass surface under a pressure of 20 dyn/cm. Following the dipping to GOD solution for ca. 1 hour, the LB film was illuminated with blue light.

Photodecomposition of I in the monolayer was monitored by optical absorption changes either in the visible ( $\sim 470$  nm) or IR ( $2120\text{ cm}^{-1}$ ) region (Fig. 4). Rapid diminishing of the azide absorptions reflects the photolysis to nitrene which is capable to attack reactive sites in the protein. After repeated rinse, relative quantity of immobilized GOD was estimated by activity measurement for glucose oxidation by use of a leuco dye-peroxidase system as an indicator.

Enzymatic activity measured as a function of adsorption time (Fig. 3) implies that the adsorption reaches to a maximum in ca. 1 hour resembling the result in Fig. 2. Radioisotope experiments with  $I^{125}$ -labelled GOD were carried out and revealed the surface density of GOD immobilized to be around  $2 \times 10^{12}$  molecules/cm<sup>2</sup>, which nearly corresponds to a close-packed monolayer of GOD molecules. Stability and amount of immobilized GOD were amply higher than those observed for inert amphiphiles such as fatty acids and esters. Actual binding reactions of I with the protein are difficult to be elucidated and are now under investigation. Glucose sensors prepared by the above technique also showed high sensitivity and will be described briefly.

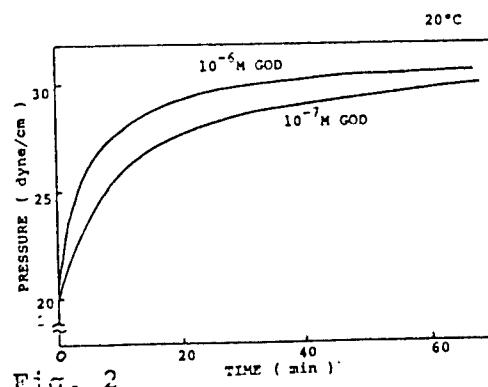


Fig. 2

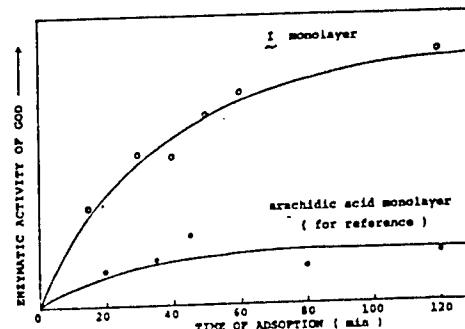


Fig. 3

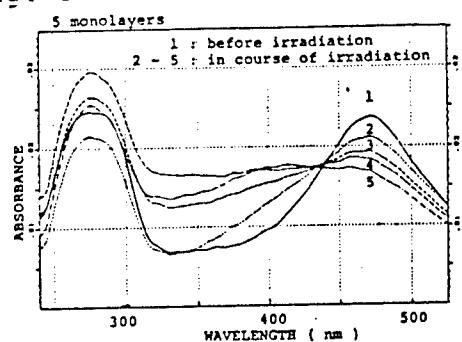


Fig. 4 (for visible region).

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# LIGHT-INDUCED ELECTRIC RESPONSES OF DRIED CHROMATOPHORE FILM

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Chromatophores are subcellular organelles of photosynthesis in photosynthetic bacteria and contain photosynthetic reaction centers (RCs) which are protein complex in a membrane and convert light energy to electric energy. We have examined photoelectric properties of the dried chromatophore film of the bacteria Rhodopseudomonas viridis and Rhodobacter sphaeroides, and reported that the film exhibited light-induced electrical transients [1] and spectrophotometric results showed that protein complex structure of the RC was still remained in the dried film [1,2].

We present here results of examination to modify the photoelectric responses of the dried film by the addition of cytochrome c.

Chromatophores from Rb. sphaeroides R-26 lacking the RC-bound cytochrome c [3] were used. Cytochrome c type III from horse heart was purchased from Sigma. Dried films of chromatophores were prepared by casting chromatophore suspension on transparent

electrodes such as vacuum-evaporated thin layer of gold on glass plates and commercially available transparent electrodes. Electrical transient of the film upon light-pulse excitation were detected with FET operational amplifiers and recorded.

Cytochrome c was added in the suspension of chromatophores from Rb. sphaeroides and the films were prepared. The incorporation of cytochrome c resulted in an increase of light-induced current and deceleration of current decay with an increase in time constant of the decay. Above effects of cytochrome c was not the case in non-redox proteins such as BSA.

Electron transfer from horse cytochrome c to the RC in physiological conditions were reported [4]. Although in this work chromatophores and cytochrome c were in non-physiological conditions, the interaction between chromatophores and cytochrome c in the film could be the case. This suggested that we could modify the photoelectrical properties of the dried chromatophore films.

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# Crystallization of actin by the adsorption to charged lipid monolayer

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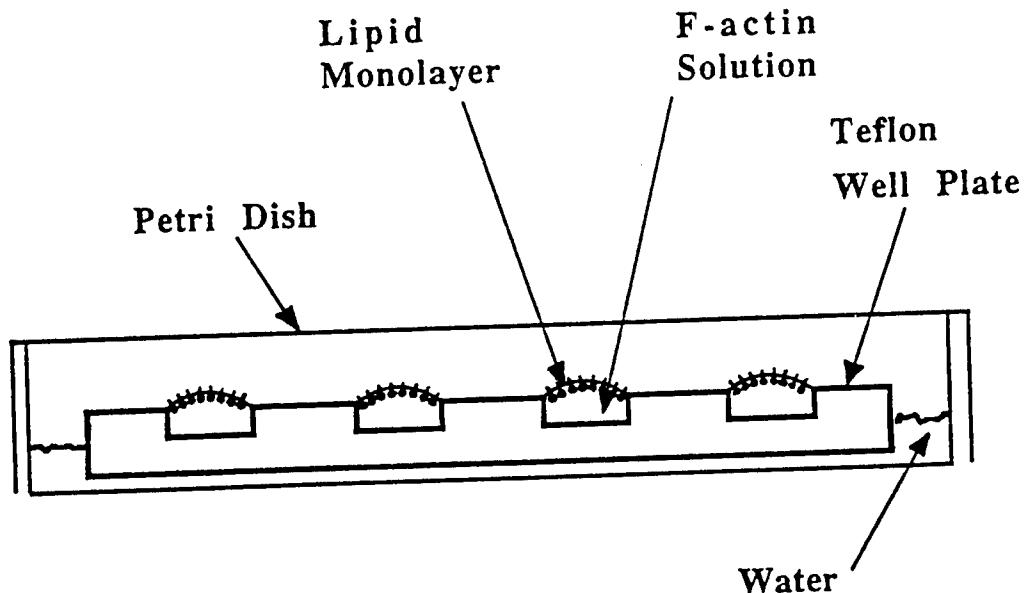
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We have been studying the three-dimensional structure of muscle protein actin to elucidate the mechanism of actin-myosin interaction and its regulation via  $\text{Ca}^{++}$  ion. Our current aim is to compare the two structures, the "activated" structure of actin thin filament which can bind myosin and the "inhibited" structure which can not bind myosin. We have already obtained actin-tropomyosin-troponin paracrystal in a solution (1). The three-dimensional molecular structure was solved by means of electron microscopy and computer image processing. The paracrystal diffracted up to 1/1.5 nm, which was not enough to reveal the intramolecular domain structure conclusively.

As a further step toward our aim, we tried to form two-dimensional actin crystal by adsorbing the F-actin (actin filament) to the lipid monolayer which had been formed at the air/water interface in advance. First 100  $\mu\text{l}$  of the buffer solution was put into each well (6 mm diameter, 2 mm deep) in a teflon plate (see the figure below). This solution contains 10 mM of  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$  (pH 7.4), 100 mM of

KCl, 50 mM of MgCl<sub>2</sub>, 0.2 mM of CaCl<sub>2</sub>, 1 mM of ATP, and 1 mM of  $\beta$ -mercaptoethanol. A slightly excessive amount of phosphatidylcholine + stearylamine solubilized in chloroform and hexane (50:50 in vol/vol) was placed on the surface of the buffer solution to form the lipid monolayer. F-actin solution (10  $\mu$ l) was subsequently injected into the buffer solution using a micro-syringe. Adsorption was facilitated by electrostatic interaction between the negative surface charge of actin and the positive charge of stearylamine incorporated into the lipid monolayer. The plate was placed in a sealed Petri dish containing water to keep humidity. Crystallization was promoted by use of highly fluid egg-yolk phosphatidyl-choline and by incubating the specimen at room temperature for an hour.



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# Nonlinear Characteristic of Lipid Monolayer in Relation to the Ability of Self-Organization

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In taste and olfaction, electrical impulses in the nerve are generated at sensory organs by chemical stimuli, that is, chemical information on chemical structure and concentration is converted into the frequency and the manner of frequency modulation of nerve impulse. In order to mimic the mechanism of molecular recognition in biological system, we have currently studying artificial excitable membranes. We have found that a rhythmic and sustained electrical oscillation is generated for a water-oil-water liquid membrane which contains sodium oleate in one of the aqueous phases. The frequency, amplitude and shape of the electrical oscillation were found to change characteristically by the addition of various taste-compounds to the aqueous phase containing sodium oleate. These characteristic changes of the oscillation to various taste-compounds is expected to be related to the nonlinear behavior of the oleate molecules at the oil-water interface.<sup>1</sup>

In order to make clear the effect of taste-compounds on the nonlinear behavior of the oleate molecules, here we have studied the dynamic characteristics of surface pressure of oleic acid at an air-water interface. Dynamic surface pressure of the

monolayer of oleic acid on an aqueous solution was measured, and the induced change of the surface pressure is continuously monitored by using platinum plate attached to an electronic balance (Fig.1). Fig.2 shows the characteristic changes of the dynamic surface pressure upon the addition of taste-compounds. This results demonstrates that taste-compounds induce marked changes in the manner of aggregation at a surface depending on their taste categories. The characteristic response to taste-compounds in the dynamic surface pressure will be discussed in relation to the characteristic effect of taste-compounds on the electrochemical nonlinearity in the presence of oleate molecules.

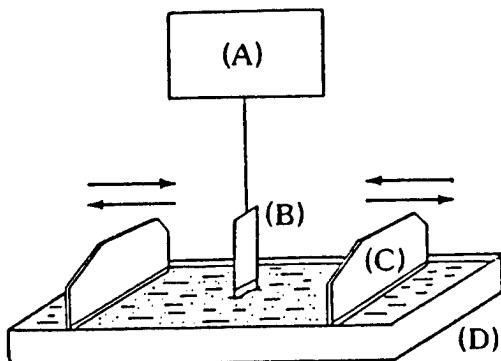


Fig.1 Diagram of the experimental apparatus used for measuring the dynamic K-A characteristics. (A) electronic balance, (B) Pt-plate, (C) teflon blade, and (D) trough.

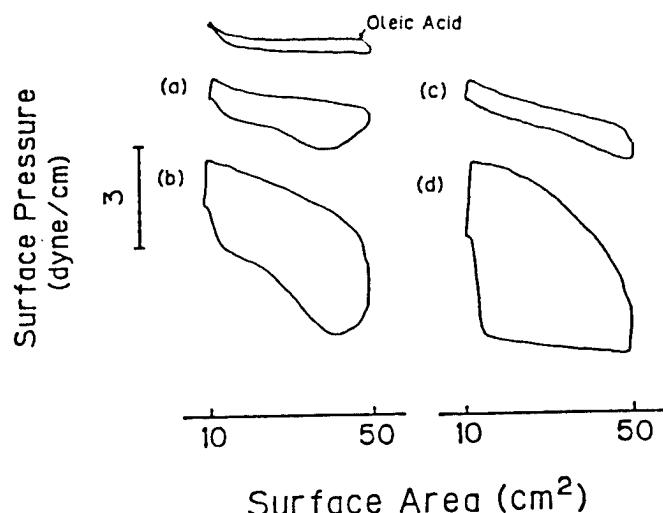


Fig.2 Characteristic change of the dynamic K-A loop caused by the addition of taste compounds to the aqueous solution which contains oleic acid. (a) 10 mM HCl, (b) 30 mM NaCl, (c) 100 mM sucrose, and (d) 1 mM nicotine.

Reference: (1) K. Yoshikawa, et al., Langmuir 4, 759-762(1988).

## Stability and Characterization of Phospholipid LB Film

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### Introduction

Phospholipids are important components of biomembranes and they are amphiphilic molecules that form the bilayer structure. To investigate the lamellar structure constructed by these molecules, so-called "oriented multilamellar" has been used. However "oriented multilamellar" is prepared only by casting the phospholipid solution onto the appropriate substrate. Another excellent method for preparing the well arranged film is Langmuir-Blodgett technique <sup>1)</sup>. This report aims to make clear the difference in the regularity of the films between the "oriented multilamellar" and LB film.

### Materials

Phospholipid was dissolved in chloroform-methanol (1:1 V/V) mixture. So-called "oriented multilamellar" of phospholipid was made by putting the solution onto the glass slide and by evaporating this under nitrogen stream. Then the trace of solvent was removed by drying in vacuum. After hydrated overnight at 100 % relative humidity and 80°C, this was served for the sample.

Thin film of phospholipid was deposited on the glass substrate by the Langmuir-Blodgett technique. DPPA (free acid, Sigma) was dissolved in chloroform. This solution was introduced onto the surface of distilled water subphase containing  $\text{CaCl}_2$   $10^{-4}$  M pH 6.9. The monolayer film of DPPA was compressed to a pressure of 40 mN/m. The substrate, micro-slide-glass (Iwaki) was inserted and pulled out vertically through the monolayer surface at a rate of 10 - 15 mm/min by manual operation. When the surface pressure was kept to 40 mN/m, multilayered Y-type films were formed and deposition ratio was about 0.9 - 1.1.

### Results

The both samples show the low angle (0,0,1) x-ray diffraction peaks due

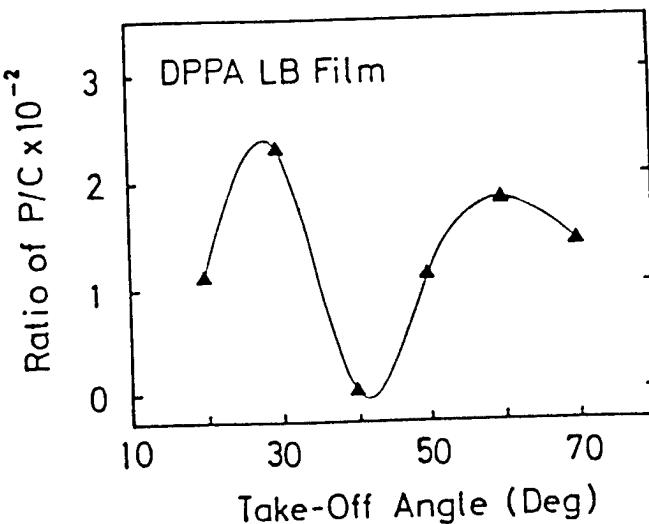
to the lamellar structure. The lamellar spacing was 53 Å for the DPPA LB film indicating the formation of Y-type film in consistent with the lengths of DPPA molecule of about 27 Å.

With the spread of the (0,0,1) diffraction band recorded by the x-ray film, the regularity spread of the both films were compared. The apparent angular variation was roughly estimated to about 17° for DPPA LB film, on the other hand, 36° for "oriented multilamellar" of DMPC. This fact demonstrates the "oriented multilamellar" is more randomly spread than the LB film.

To characterize the DPPA LB film and "oriented multilamellar", electron spectroscopy for chemical analysis (ESCA) was used. The chemical composition at the various depth from the surface of the DPPA LB film was estimated by the take-off angle dependence of bombarding x-ray beam. As the take-off angle is larger, the chemical composition at deeper part of the film is observed. Figure shows the take-off angle dependence of P/C ratio for 5 layers DPPA film. There are two maximum points of the P/C ratio. The high P/C ratio corresponds to the head part of DPPA molecule because this molecule consists of the hydrophilic head part containing a P atom and hydrocarbon chain with many C atoms. The take-off angle dependence of P/C ratio indicates that the regular layer structure is constructed.

The P/C ratio of the "oriented multilamellar" of DPPA was 0.021 at 45° of take-off angle. This value is in agreement with the P/C ratio of DPPA molecule ( $1/35 = 0.029$ ) indicating that DPPA molecule is randomly distributed at least on the surface of the "oriented multilamellar".

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1092-1097.



Figure

## ION-CHANNEL SENSORS BASED ON LANGMUIR-BLODGETT MEMBRANES

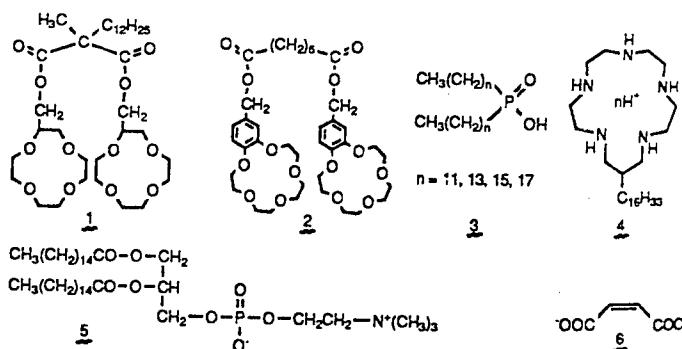
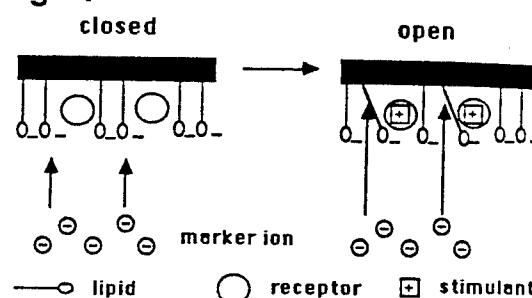
Masao Sugawara, Masamitu Kataoka, Hiroyuki Sazawa, Shinobu Nagase, Ryuichi Naganawa and Yoshio Umezawa  
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The selective and sensitive processes of molecular recognition and signal transduction/amplification in biological membrane systems seem to provide the sound basis for the development of new types of chemical sensors. We have been trying to take advantage of the unique characteristics of ion-channel phenomena in view of the development of new chemical sensors.

In the present paper, we will discuss the principle and actual constructions of the proposed ion-channel sensors based on Langmuir-Blodgett molecular assemblies.

The present sensor has a function of model channel switching by the following sequence. i) In the absence of a stimulant (analyte), the channel is closed and therefore, marker ions (monitoring ions) can not permeate through the membrane(Fig. 1a). ii) With the stimulant, the channel is opened, and the marker ion is allowed to permeate through the membrane, which is immediately detected electrochemically at an underlying electrode. The amount of marker ions thus detected is a direct but much amplified measure of the stimulant. For the selective recognition of an analyte(stimulant) at the surface of the LB molecular assemblies and the resulting control of the membrane permeability for marker ions

**Fig. 1**



with the stimulant, we need to incorporate some kind of recognition sites at the surface of the membrane, that interact specifically with a stimulant to open the model channels for marker ions. This is achieved by two approaches: i) direct interaction of a stimulant with the active receiving sites of membrane molecules itself or ii)selective interaction of a stimulant with an appropriate receptor incorporated as a separate molecular entity on/in the membrane surface.

## Cation Responsive Ion-Channel sensors

Bis(12-crown-4) 1 as a  $\text{Na}^+$  ion receptor, and valinomycin and bis(15-crown-5) 2 as  $\text{K}^+$  ion receptors were embedded in the LB membrane of dialkyl phosphate 3. The cyclic voltammetric response of the sensor based on the composite membrane with a 1:1

receptor/lipid molar ratio was investigated. With the sensor based on bis(12-crown-4) 1 and dihexadecyl phosphate, the channel switching by  $\text{Na}^+$  ion (analyte) is observed as a shift in the peak potential accompanying an increase in the peak current of anodic wave due to the permeated  $[\text{Fe}(\text{CN})_6]^{4-}$  ions (Fig. 2). The important feature of the ion-channel sensors is that selective interaction of an analyte at the membrane surface and the resulting change in membrane permeability towards appropriate marker ion are used as a measure of signal transduction and amplification. The (minimum) amplification factor is defined as the relative moles of permeated marker ions to the total moles of receptor embedded in the outmost layer of the LB membrane. Amplification factors thus obtained for some cation responsive ion-channel sensors is given in Table 1.

**Anion Responsive Ion-Channel Sensors**  
The sensor is based on lipophilic macrocyclic polyamine 4 as an anion receptor embedded in the LB membrane of dipalmytoylphosphatidylcholine 5 with a 1:1 receptor/lipid molar ratio. Cyclic voltammetric detection of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy: 2,2'-bipyridyl) used as a marker ion for the sensor is shown in Fig. 3. In the absence of guest anion, permeation of the marker cation was suppressed by a condensed positive charge of the protonated macrocyclic polyamine. By adding maleate anion 6 as a stimulant, the model channel is opened by neutralization of the membranous positive charge due to the selective complexation of protonated polyamine with the guest anion. The anion responsive sensor discriminates positional isomers of phthalate in the following increasing order of response: phthalate < isophthalate < terephthalate. The sensor also discriminates the following nucleotides in the order:  $\text{AMP}^{2-} < \text{ADP}^{3-} < \text{ATP}^{4-}$ .

Fig. 2

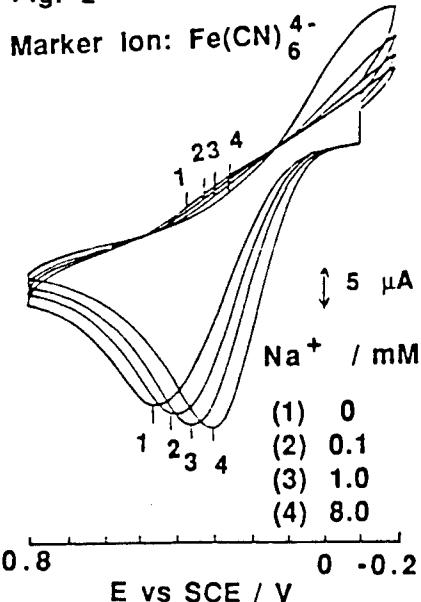


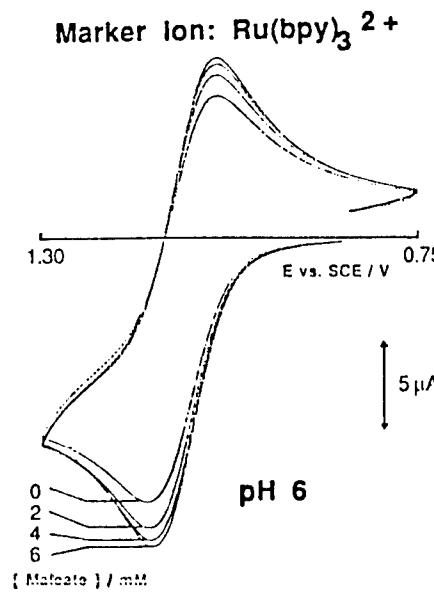
Table 1 Degree of Amplification with some Ion-Channel Sensors

Membrane materials <sup>a)</sup>	Marker ions	Stimulant	Amplification <sup>b)</sup>
$(\text{C}_{18})_2\text{PO}_4\text{H}$ plus bis(12-crown-4)	$\text{Fe}(\text{CN})_6^{4-}$ 1 mM	$\text{Na}^+$ 8 mM	4.1
$(\text{C}_{12})_2\text{PO}_4\text{H}$ plus valinomycin	$\text{Fe}(\text{CN})_6^{4-}$ 1 mM	$\text{K}^+$ 8 mM	4.5
$(\text{C}_{12})_2\text{PO}_4\text{H}$ plus bis(15-crown-5)	$\text{Fe}(\text{CN})_6^{4-}$ 0.2 mM	$\text{Na}^+$ 8 mM	1.1

a) The molar ratio of receptor to lipid is 1:1.

b) Defined as the relative molar ratio of permeated marker ion to the total moles of receptor.

Fig. 3

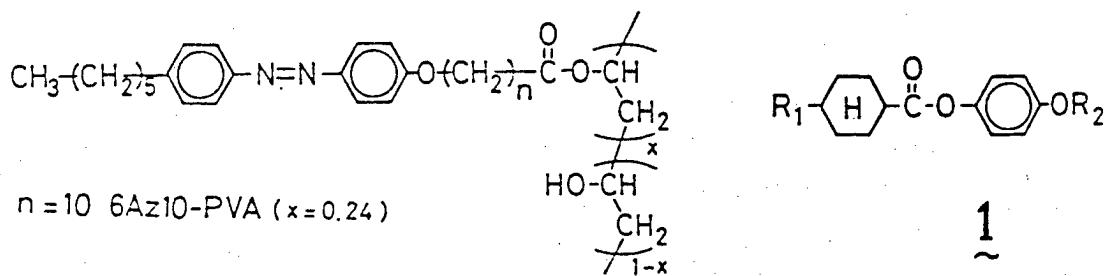


Reversible Photochemical Alignment Control of Nematic Liquid Crystals by "Command Surface". Quartz Surface Modified with Azobenzene Polymers Deposited by Langmuir-Blodgett Technique.

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**Introduction** In the previous papers, we have reported alignment changes of nematic liquid crystals (LC) induced by photochromic azobenzene layers on the substrate surface (command surface).<sup>1</sup> To elucidate in more detail the mechanism of the alignment changes triggered at the surface, it is desirable to obtain defined monolayer surfaces. In this context, we attempted to employ LB technique for surface modification of the substrate. Poly(vinyl alcohol)s containing azobenzene (Az) side chains (6Az10-PVA) were used for film forming materials because Az units in these LB films maintain high reactivity of trans/cis photoisomerization.<sup>2</sup> Correlation between the film structure and alignment responses of nematic LC 1 is presented.



**Experimental** Monolayers of (6Az10-PVA) were deposited onto quartz substrates using a Lauda film balance. LC 1 (C-17-N-73-I) was sandwiched between the two substrate (cell thickness 8  $\mu\text{m}$ ). LC alignment changes were observed by monitoring intensities of transmitted He-Ne laser beam in the method described elsewhere.<sup>1</sup>

**Results and Discussion** Reversible LC alignment changes, parallel  $\rightleftharpoons$  homeotropic, were observed upon alternate exposure of the

cell to u.v. (365 nm) and visible (436 nm) lights (Fig.1). Clearly these changes are induced by the cis  $\rightleftharpoons$  trans photoisomerization of Az units of the deposited film. One layer was sufficient to cause this effect, suggesting that, even in the case of multilayers, the surface layer "commands" the alignment.

Fig.2 indicates the relationship between the area per Az unit ( $A$ ) and wettability ( $\theta$ : contact angle for water) for the monolayer films of 6Az10-PVA. Two kinds of substrates were used, clean and ethyl-silylated quartz plates. Alignment responses were observed when  $A$  was less than  $1 \text{ nm}^2$  for both plates irrespective of the magnitude of surface energy. This implies that the responding behavior is primarily determined by two dimensional density of Az unit and that thermodynamical arguments are less important in the present LC/LB film system.

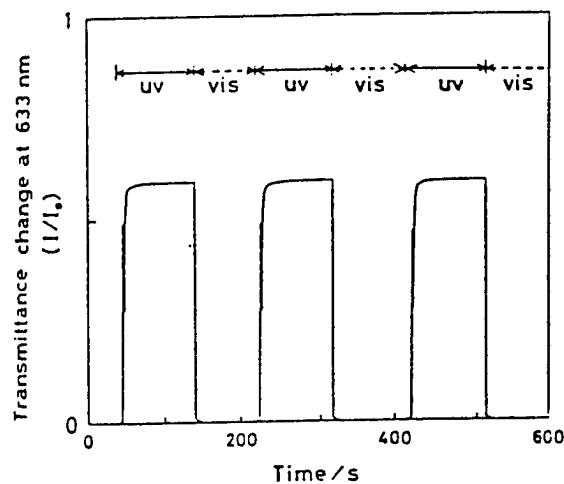


Fig.1 Reversible transmittance changes of He-Ne laser light through LC cell between two crossed polarizers upon alternate exposure to u.v. and visible lights.

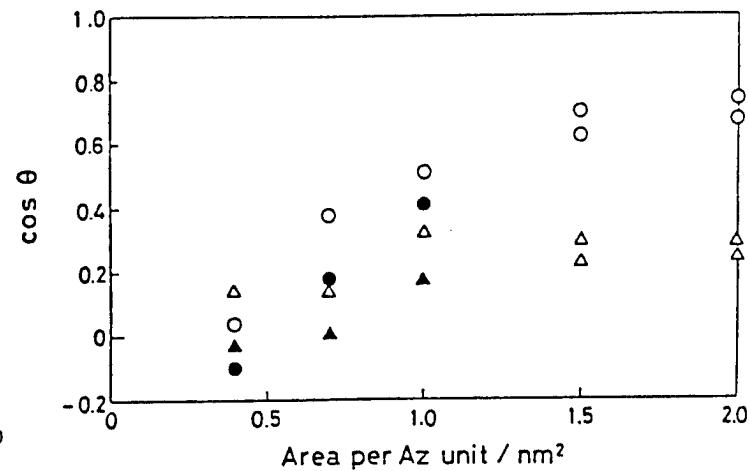


Fig.2 Contact angle for water as a function of two dimensional Az density on substrate. The monolayer was deposited onto clean (circles) and silylated (triangles) quartz plates. Of the pairing two points, the upper and the lower are data for cis and trans Az surface, respectively. Open and closed symbols indicate LC alignment of parallel and homeotropic, respectively.

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# PHOTOSENSITIVE POLYIMIDE LB FILM DERIVED FROM 4-(17-OCTADECENYL)PYRIDINE AND POLYAMIC ACID

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## 1. Introduction

From a process standpoint it is desirable that thermally stable LB films<sup>1,2,3)</sup> are photosensitive and fine patterns are easily fabricated in these films. We used a mixture of polyamic acid (PA) and 4-(17-octadecenyl)pyridine (ODP) and showed that a negative type photosensitive LB film was obtained<sup>4)</sup>. We will report here the effect of the main chain molecular weight and the presence of a double bond and a pyridine ring in a side chain on the exposure characteristics of the PA + ODP mixture LB film and we will demonstrate the fine patterns fabricated in these LB films.

## 2. Experimental

Polyamic acids with two different molecular weights were synthesized from pyromellitic anhydride and 4,4'-diaminodiphenylether (PA1:Mn = 1,380, Mw = 2,780, PA2:Mn = 7,080, Mw = 10,900). ODP was purchased from Wako Pure Chemical Industries, Ltd. Each substance was dissolved into a 1:1 dimethylacetamide (DMAc) and benzene (Bz) solution. Final concentration of the mixed solutions is 1.6mM PA monomer unit and 3.3mM ODP for either high and low molecular weight PA.

Both mixtures could be deposited on various substrates at 25mN/m by the LB technique. Deep UV light was irradiated using Canon PLA-521F contact printer equipped with cold mirror CM 250. Development was carried out by soaking the substrate in a 1:1 DMAc and Bz solution for 1 min, and then in ethanol for 1 min. Imidization was carried out by the chemical treatment<sup>2)</sup>. Fine patterns were fabricated through a photomask in 10 layers LB films on a silicon substrate whose top was covered with 100 Å thermally grown silicon dioxide.

## 3. Results and Discussion

The limiting area per PA monomer unit calculated from the isotherms are 91Å<sup>2</sup> for the both molecular weight PA, while that per ODP is 43Å<sup>2</sup>. Those values obtained from the molecular models are c.a.100 Å<sup>2</sup> and 20Å<sup>2</sup>, respectively. From this we concluded that PA molecules are floating at the air-water interface and ODP hydrocarbon chains are resting on the flat rings of PA. Thicknesses per layer for ODP+PA1 measured by ellipsometry are 17Å after the deposition, 15Å after 5 min deep UV irradiation, 6Å after the development and 4Å after the imidization. In FTIR spectra, peaks assigned to CH<sub>2</sub> disappeared and those typical

to imide appeared after the imidization, which clearly shows complete conversion of the precursor into polyimide.

Fig. 1 shows the exposure characteristics of the two ODP + PA mixtures. The gel point is lower for the high molecular weight PA but both normalized thicknesses saturate to 35%-42%. In order to check the effect of main chain scission on the exposure characteristic, molecular weight change of PA2 by the deep UV irradiation was measured by gel permeation chromatography. The degradation was not remarkable (only 10% molecular weight decrease after 30 min irradiation), therefore the saturation is due to a side reaction of the mixture.

The effect of a double bond and a pyridine ring was checked by using model compounds. The LB film of the octadecylpyridine + PA mixture and that of  $\omega$ -tricosenoic acid did not remain after the development. This shows that both a double bond and a pyridine ring are necessary to bring about a crosslinking reaction. A low acceleration energy (1KV) SEM photo of the fine patterns fabricated in the LB films are demonstrated in Fig.2. It has been found that liquid crystal molecules are aligned along these grooves and details of the molecular orientation control by these grooves are now under investigation.

#### Acknowledgements

The authors are grateful to Mr. Higashine and Mr. Henmi of Wako Pure Chemical Industries, Ltd., for their help in synthesizing ODP. They are also grateful to Dr. Matsui and Mr. Kojima of NEC Corporation for their help in taking SEM photos.

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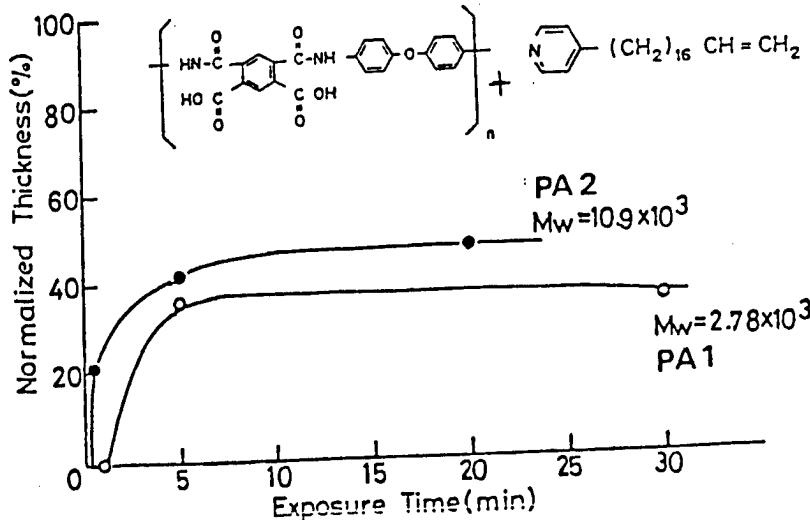


Fig. 1 Exposure Characteristics of ODP + PA

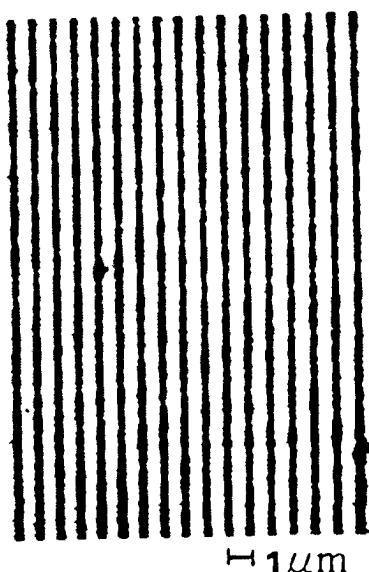


Fig. 2 SEM Photo of Fine Patterns Fabricated in ODP + PA1 LB Film (5min Exposure)

## The Preparation of High Quality Y-type Polyimide LB Films

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Recently there has been much interest in ultra thin films of polyimide (PI) derived from polyamic acid LB films, because of their potential use as insulating layers in electronic devices (1) and as aligning layers for liquid crystal displays (2).

It is not possible to deposit PI films directly by the LB deposition technique as the molecule does not possess the necessary amphiphilic nature. This problem is circumvented by using a polyamic acid/alkyl amine salt which forms stable L-films and can be deposited by the LB technique. The polyamic acid salt LB film is then converted to polyimide and the hydrocarbon chains removed by a solvent treatment (3).

In previous reports it was noted that these films were found to deposit Z-type or to start Y-type and convert to Z-type. In our work we have developed a preparation method for producing Y-type films of PI. This preparation method has led to films of higher quality as true Z-type deposition is rarely accomplished and could often be better described as poor Y-type depositon. The quality of the film is important, as it can be a major factor in determining whether a particular application can be successfully implemented or not.

The key to obtaining Y-type depositon is to ensure the correct balance between the hydrophobic and hydrophilic parts of the molecule. We achieved this by carefully controlling the age of the spreading solution, and the pressure annealing time of the L-film prior to deposition. Further improvement was achieved by optimising the materials used.

The difference in the quality of the Y-type and Z-type layers can be demonstrated by their aligning effect on nematic liquid crystal materials, which are a sensitive indicator of the quality and degree of alignment of the prepared surface. Figure 1.a and 1.b show the textures observed for homogeneously aligned nematic liquid crystal cells for Y and Z-type alignment layers respectively. The texture imparted by the Y-type films is very clearly superior to that imparted by the Z-type films.

Other LC cell properties were also significantly different. Light transmission data taken for two cells, one aligned with Y-type alignment layers the other with Z-type alignment layers, placed between crossed polarizers and oriented at 0° and 45° with respect to the analyser, is summarized in table 1. Figures for areas aligned with different numbers of layers are also given.

The difference in contrast is clearly greater for the

Y-type films. Also it should be noted that the contrast and texture quality both increase with the number of deposited layers for the Y-type alignment cells, which we attribute to the isolation of the ITO surface as this is known to have a disruptive effect on the alignment. This result is in contrast to other reports, where a peak in the contrast was observed for 5 aligning layers. The variation in the contrast with number of layers for the cells aligned with Z-type layers is due mainly to the poor quality of the texture.

Structural characterization was also carried out using SEM, TEM and IR. These results showed the Z-type films to have many deposition defects and thus to be of lower structural integrity than the Y-type films. This supports the original assumption that the Z-type deposition observed is actually poor Y-type deposition and that to achieve high quality films Y-type deposition is preferable.

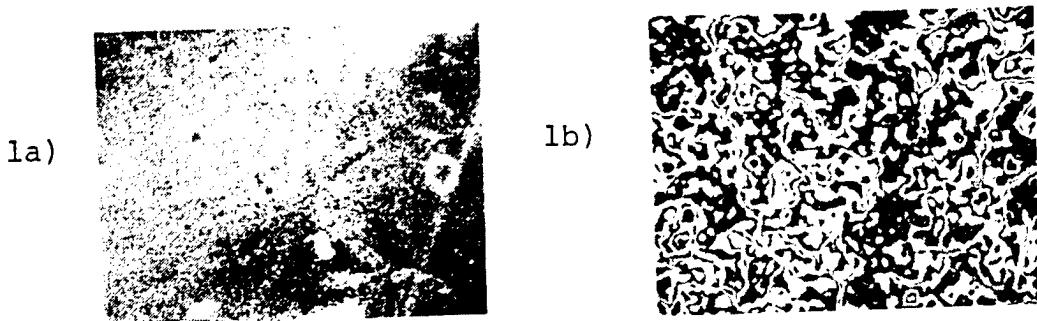


Figure 1a,b Nematic textures for a) Y and b) Z-type films

Table 1 Transmission values for nematic cells aligned using Y and Z-type alignment layers

		NUMBER OF LB LAYERS			
		1	3	5	9
Y-TYPE	45°	17%	73%	75%	90%
	0°	5%	5%	5%	0%
Z-TYPE	45°	10%	68%	72%	60%
	0°	8%	18%	12%	23%

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## APPLICATION OF POLYIMIDE LB FILMS TO DEEP UV RESISTS

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In order to improve the heat-stability of LB films, we developed a new process to obtain ultrathin polyimide LB films by using a new polyimide precursor (1).<sup>1)</sup> The resultant films have heat-stability above 400°C and good insulation properties acceptable for electronic devices.

We have extended our study to the patterning of LB films, which is necessary for their application in electronic devices. We have synthesized a new photosensitive amphiphilic polyimide precursor (2) with double bonds.

The precursor 2 mixed with octadecyl alcohol and benzoin ethylether (molar ratio 3:3:1) gave a stable monolayer on an air/water interface. The limiting area was 25 Å/unit and the collapsed pressure was 40 mN/m.

Y-type multilayer films of the above mixed monolayer have been easily obtained by the LB technique at a surface pressure of 25 mN/m with a dipping speed of 10 mm/min. Silicon wafers whose surface was hydrophilically treated were used as solid plates. The monolayer thickness and refractive index were evaluated to be 22 Å and 1.55, respectively, by ellipsometry.

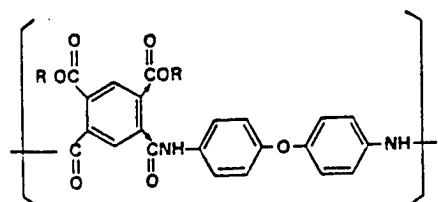
All exposures were carried out with a low pressure mercury lamp (254 nm) as a deep UV light source. After exposure, the multilayers were developed in chloroform/dimethylacetamide (4:1 in volume) and rinsed in ethanol. Figure 1 shows plots of the normalized thickness vs. exposure energy. At first the thickness increases as the exposure energy increases, which means that the films work as negative resists. In the FT-IR spectrum the characteristic absorptions based on double bonds disappear upon exposure, which indicates that cross-linkings occur between double bonds. The sensitivity defined at a normalized thickness of 0.7 is 350 mJ/cm<sup>2</sup>.

Interestingly, the thickness decreased at above 1.2 J/cm<sup>2</sup> exposure energy. This suggests decomposition of the polymer

chain.

After the above mixed multilayers (21 layers) were exposed through a photomask in contact mode, development of the films in chloroform/dimethylacetamide (4:1 in volume) gave a negative pattern. A resolution of 0.5 um space and 1.0 um line has been achieved. Furthermore, silicon substrates were dry etched with a mixed gas of  $\text{CF}_4$  and  $\text{O}_2$  through the mask of the patterned LB films. The LB films (31 layers, 690 Å) were not destroyed while single crystal silicon was dry etched to the depth of 2.5um. The etching rate is evaluated to be 320 times lower than that of silicon. Even when the thickness of the LB films is small, the films have been found to have high resistance to dry etching.

In conclusion, the new LB films have good sensitivity, good resolution and excellent resistance to dry etching. They are expected to be promising deep UV photoresists for 16 and 64 M VLSI and they have the potential to work as KrF excimer laser (248 nm) resists.



(1) R:  $\text{CH}_3(\text{CH}_2)_{17}-$   
(2) R:  $\text{CH}_2=\text{CH}(\text{CH}_2)_{15}-$

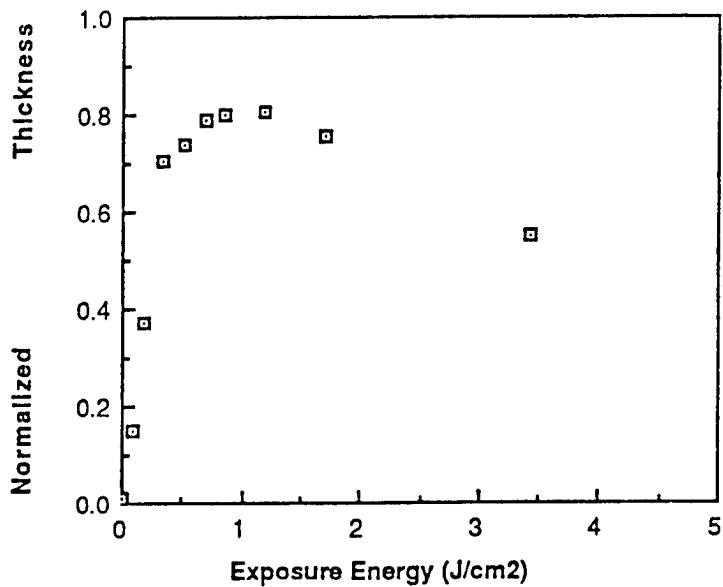


Figure 1. Sensitivity Curve

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## Study on the Concentration of Immobilized Enzyme by L.B.films.

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The urease is an enzyme which decomposes urea into  $\text{NH}_3$  and  $\text{CO}_2$ . We can produce an urea sensor by immobilizing urease on the  $\text{pH}$  sensor (e.g. ISFET), and the L.B. method has been expected to be useful as one the immobilizing methods. We have measured for the first time the amount of urease adsorbed to L. film, and have shown that the relation between the amount of adsorbed urease and the concentration of enzyme in the solution can be expressed by an equation similar to the Langmuir's adsorption isotherm.

The amount of adsorbed urease was estimated by U.V.spectroscopy. Lambert-Beer's law shows the absorbance A to be proportional to the thickness of solution 'L' and concentration 'C'.

$$K \cup A / L \dashrightarrow \dots \quad (2)$$

As for L.B. films, the thickness of solution is equivalent to the thickness of the films, and it can be estimated from the transfer ratio. Accordingly, if the relationship between the absorbance and transfer ratio is linear, the slope will indicate the relative concentration of urease adsorbed to L.film on water.

The charged state of urease is negative when the pH of solution is between 6 and 7, and the adsorbent must be charged positive so as to be able to adsorb the urease. We used stearylamine as the adsorbent. The urease adsorbed films were deposited on quartz glasses by use a trough divided into 3 compartments. The absorbance at  $\lambda=280$  nm were measured at intervals of 15 min. during breaks in the deposition. Dipping speed was 50mm/min. on downstroke, 5mm/min on upstroke, and the perfect deposition required 30min of drying. The type of deposition was X-type, and the surface of L.B. films were hydrophilic.

Fig 1. shows that the relationship between the transfer ratio and absorbance is linear, accordingly the urease is adsorbed uniformly and we can estimate the relative concentration of urease adsorbed to the L.films on water. The relation between the reciprocal slopes (relative adsorbed concentration) and reciprocal concentration is shown by two straight lines for each adsorption time, which both originates from the same point on the Y-axis (Fig 2.). This fact shows that the adsorption of urease can be described by an expression like Langmuir's adsorption isotherm.

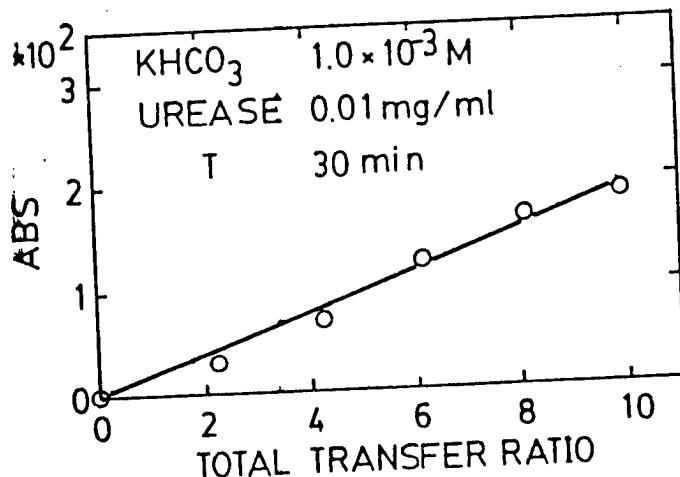
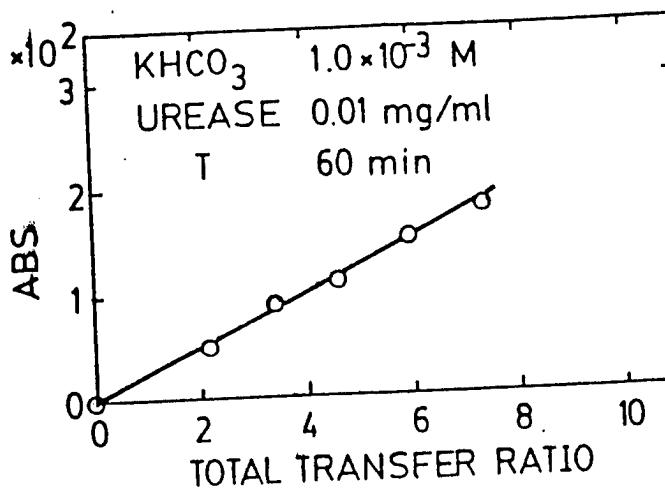


Fig.1- Absorption of a immobilized urease as a function of the transfer ratio.

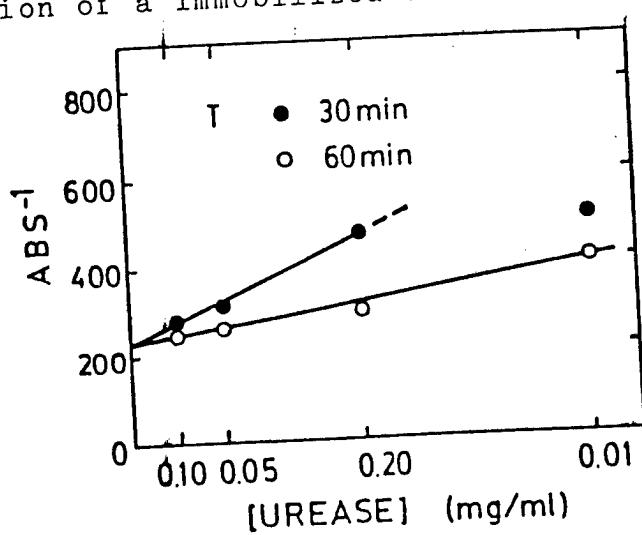


Fig.2- Reciprocal absorption as a function of urease concentration.

Dry Formation of Fatty Acid Crystallized Thin Film and Application

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Crystalline thin films were attractive for both fundamental research and applications such as a resist for fine pattern fabrication, a thin insulator, and a functional thin film. Crystalline films could be formed by both wet and dry method which are Langmuir-Blodgett technique and vacuum evaporation. In this paper crystalline film formation by evaporation and its application as a resist were described using stearic acid [ $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ :mp=70C],  $\omega$ -heptadecenoic acid [ $\text{CH}_2=\text{CH}(\text{CH}_2)_{14}\text{COOH}$ :mp=55C], and  $\omega$ -tricosenoic acid [ $\text{CH}_2=\text{CH}(\text{CH}_2)_{20}\text{COOH}$ :mp=76C].

Crystalline films of the monomers were formed by evaporation under conditions in Table 1. Crystallized film structures were evaluated by X-ray diffraction using Cu-K $\alpha$  radiation. The diffraction patterns showed only peaks characterized (0,0,L) of fatty acids and the experimental values of interplaner spacings were agreed with theoretical values.

Table 1 Oriented Film Formation Using Various Monomers by Evaporation

monomer	melting point (°C)	evaporating conditions furnace temperature (°C)	substrate temperature (°C)	film characteristics structure by X.D.	thickness (Å)	interplaner spacing (Å)
$\omega$ -hepta-deenoic acid	55	100	35	crystal	5000	37.2
stearic acid	70	100	35	crystal	2000	39.3
$\omega$ -tricosenoic acid	76	120	40	crystal	2000	49.1

As the resist process, the double layer resist using oriented fatty acid and Al film was proposed for total dry process as shown in Fig. 1. In this study, electron beam delineations and thermal developments were performed at an acceleration voltage of 5kV. The sensitivity of stearic acid was about  $300-500\text{uC/cm}^2$  which was lower than those of other two monomers because stearic acid was a saturated monomer. The selfdevelopment was observed in stearic acid film when the exposure dose was high. For  $\omega$ -heptadecenoic acid and  $\omega$ -tricosenoic acid, the sensitivities were almost same. When  $\omega$ -heptadecenoic acid film was used, the substrate was elevated by a joule heating of the electron beam current at a large dose rate and a part of film was vapourized. At an exposure dose of  $280\text{uC/cm}^2$ , 2μm line width patterned on the stearic acid film was successfully developed thermally as shown in Fig. 2.

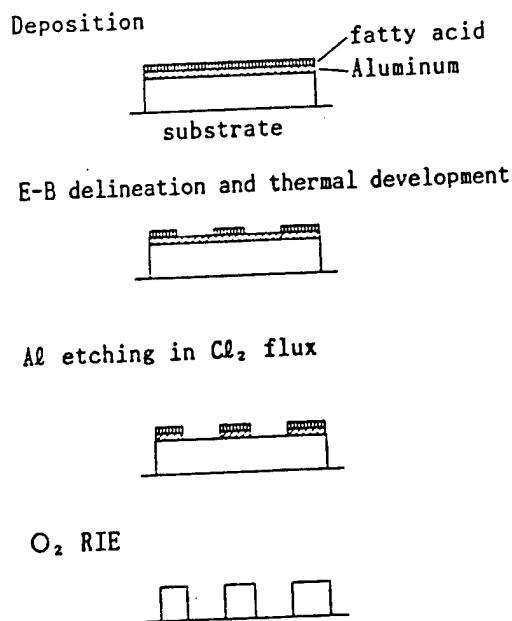


Fig.1 Double layer resist process using fatty acid and Al

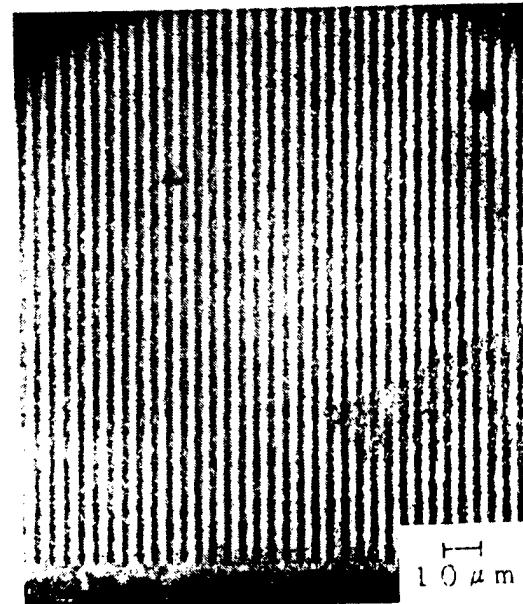


Fig.2 Photomicrograph of 2μm negative pattern of Stearic acid developed thermally